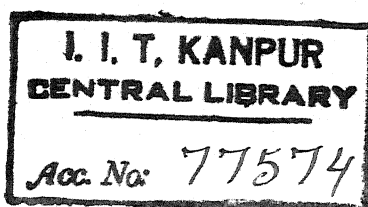


**A : HARTREE-FOCK-SLATER WAVE FUNCTIONS AND
MAGNETIC PROPERTIES OF ATOMS AND IONS
AND**

**B : SATURATION IN MULTILEVEL-MULTIRESONANCE
ZEEMAN SYSTEMS : A THEORETICAL STUDY**

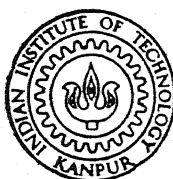
A Thesis Submitted in partial fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY



BY

K. M. S. SAXENA

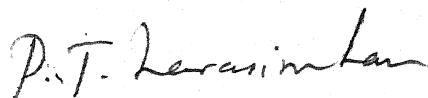


**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

DEDICATION

This thesis is dedicated to my parents.

Certified that the work presented in this thesis has
been done by Mr. K.M.S. Saxena of the Physics Department,
Indian Institute of Technology, Kanpur under my supervision.



P.T. Narasimhan

Professor

Department of Chemistry
Indian Institute of Technology
Kanpur

ACKNOWLEDGEMENTS

I wish to take this opportunity to put on record my deepest thanks to Professor P.T. Narasimhan not only for his suggesting the problems and valuable guidance but also for his ready advice and constant encouragement throughout this work.

To Professor G. Malli, Professor C.J. Lenander and Professor R.M. Sternheimer go many thanks for providing some of the results of their investigations prior to publication and also for some stimulating private communications.

I would like to express my appreciation for the helpful cooperation of the staff of the Computer Centre, Tata Institute of Fundamental Research, Bombay, where some of the calculations were performed. Thanks are also due to Messers R.N. Basu, R.S. Hitkari, S.G. Ravi Kumar and S. Kapoor of the Computer Centre of this Institute for their valuable cooperation.

I wish to thank Professor P. Venkateswarlu, Professor J. Mahanty and Professor B. Deo of the Physics Department, Indian Institute of Technology, Kanpur for their kind interest in this work.

I also wish to thank my colleagues who have helped me in many respects. In particular I wish to thank Messers P. Chandra, N.K. Ray, J. Subramanian, R.K. Gupta, Dinesh and M.S. Gopinathan for their kind cooperation.

Particular thanks are due to my wife, Nirmala for her forbearance.

Finally, it is a pleasure to thank Mr. R.D. Tripathi for undertaking the typing of this thesis with patience and interest and Mr. Ashok Bhargava for preparing the diagrams.

K.M.S. Saxena
K.M.S. Saxena

Department of Physics
Indian Institute of Technology
Kanpur

PREFACE

The thesis contains two independent parts. A brief account is given below separately of each of these parts.

Part A: Hartree-Fock-Slater Wave Functions and
Magnetic Properties of Atoms and Ions.

The purpose of this part of the thesis is to study some physical properties of many electron systems using Hartree-Fock-Slater (HFS) wave functions of Herman and Skillman and consequently to provide a set of tests to these wave functions. This part consists of six Chapters and an Appendix.

Chapter I briefly reviews the Hartree and Hartree-Fock self-consistent-field (SCF) methods. The merits and demerits of these methods are discussed particularly from the point of view of machine computation. Valuability of approximations in the Hartree-Fock scheme from the standpoint of computation time is recognized and accordingly a description of the HFS formalism which is based on a modified form of Slater free-electron exchange approximation for the exchange potential is presented. Some of the inherent limitations of the HFS formalism are also discussed here. In spite of the approximate nature of the HFS wave functions it is believed that these are reasonably close to the Hartree-Fock (HF) wave functions. A discussion of the recent developments suggesting the use of a reduced Slater free-electron exchange potential is also included in this chapter.

For reasons of simplicity, the HFS formalism of Herman and Skillman ignores the multiplet structure arising from the open-shell configurations and uses a single determinantal wave function both for closed-shell and open-shell systems. In view of the belief that the HFS

wave functions are good for closed-shell systems, calculations of diamagnetic susceptibility (χ_{HFS}) and nuclear magnetic shielding constant (σ_{HFS}) for all the rare gas atoms have been done using 110-point mesh HFS wave functions from the work of Herman and Skillman. These are presented and are compared with the results of available Hartree (H) and Hartree-Fock (HF) calculations and the experiments wherever possible. The χ_{HFS} values are in good agreement with χ_{HF} and χ_{exptl} , but σ_{HFS} values are uniformly slightly higher than the corresponding σ_{HF} values. Available data on $\sum \langle r^2 \rangle$ and $\sum \langle 1/r \rangle$ for Ne, Ar and Kr corresponding to the use of the reduced Slater free-electron exchange potential are utilized to assess the comparative usefulness of reduced Slater potential scheme. A part of the work reported in this Chapter has been already published¹.

In an attempt to have a check on the reliability of the HFS wave functions also for ions having closed-shell configuration χ_{HFS} and σ_{HFS} values were calculated for ^{the} following six isoelectronic series: He, Li⁺, Be⁺⁺, B⁺⁺⁺; F⁻, Ne, Na⁺, Mg⁺⁺, Al⁺⁺⁺; Cl⁻, Ar, K⁺, Ca⁺⁺, Sc⁺⁺⁺; Br⁻, Kr, Rb⁺, Sr⁺⁺, Yt⁺⁺⁺; I⁻, Xe, Cs⁺, Ba⁺⁺, La⁺⁺⁺; At⁻, Rn, Fr⁺, Ra⁺⁺, Ac⁺⁺⁺. In order to avoid errors which might result due to the use of a coarser 110-point mesh, 441-point mesh wave functions were used in these calculations. A Herman-Skillman type Computer program was used on IBM 7044 computer to generate these 441-point mesh wave functions. The HFS wave functions for doubly-charged and triply-charged negative ions could not be obtained due to lack of convergence. This is believed to be due to the problem of obtaining bound states in such systems. The results obtained are reported and compared with other available H and HF results in Chapter III and these are also found to have trends similar to those of rare gas atoms reported

in Chapter II. Values of various one-electron $\langle 1/r \rangle_{\text{HFS}}$ and $\langle r^2 \rangle_{\text{HFS}}$ integrals are also reported here. Since χ and σ are respectively proportional to $\sum_i \langle r_i \rangle^2$ and $\sum_i \langle 1/r_i \rangle$, it is inferred that for the closed-shell configurations the HFS wave functions are better for large r values than for small r values. Based on the general trends of the σ_{HFS} values^e reported in this chapter, a closed empirical relation is obtained and used to extrapolate the σ_{HFS} values for neutral atoms and singly, doubly and triply charged positive and negative ions from $Z = 2$ to $Z = 100$. The values extrapolated thus compare favourably with those obtained by direct calculation using HFS wave functions. Chapter III also includes a discussion of an alternative method of evaluating the σ_{HFS} values for various isoelectronic series. This method is based on the concept of stability of SCF wave functions under one-electron perturbations and the Z -expansion of the total energy values using the Z -dependent perturbation theory in the isoelectronic series. Since total HFS energy values are not available readily, the method has been demonstrated using HF energy values in an Appendix where σ_{HF} values for neutral atoms and singly, doubly and triply charged positive and negative ions in various isoelectronic series containing two to twentyseven electrons have been evaluated and presented. Use is made of the HF total energy values reported by Clementi in his work on analytic HF wave functions of positive ion isoelectronic series including neutral atoms. The σ_{HF} values obtained here seem to be as good as those obtained by direct calculation using the HF wave functions. This procedure seems to support the empirical method formulated earlier for the extrapolation of σ_{HFS} values for atoms and ions. A part of the work presented in this Chapter is scheduled to be published² shortly.

Chapter IV concerns with the presentation and discussion of

calculations of Fermi Contact interaction term (a_c , the hyperfine-structure constant) for ground states of Li, Na, K, Cu and Ca^+ using the HFS wave function for the s-orbital corresponding to the unpaired valence electron in each of them. The HFS wave functions are restricted in the sense that their m_s dependence has been ignored. Contributions to the hyperfine-structure constant a_c from the paired s-electrons of the core are therefore zero in the HFS formalism and thus core polarization is neglected. The results are compared to other calculations and quite surprisingly it is found that, in general, they agree better than both HF and UHF (unrestricted Hartree-Fock) results with the experimental data wherever available. A discussion of this behaviour is given and it is concluded that the agreement between the HFS results and the experiments is fortuitous.

In Chapter V, the results of calculations of χ_{HFS} and σ_{HFS} values for some open-shell configurations in three different regions of the periodic table are presented. These regions are (i) $Z = 3$ to $Z = 15$, (ii) $Z = 45$ to $Z = 53$ and (iii) $Z = 81$ to $Z = 91$. From a comparison between these values and the other available values it is found that the single determinantal HFS wave functions are capable of reproducing the χ and σ values to a good degree of accuracy for open-shell configurations also. The agreement for χ_{HFS} values is, however, better than for σ_{HFS} values, the latter being always slightly higher than the corresponding σ_{HF} values. The HFS wave functions used here are non-relativistic and relativistic corrections are needful for large- Z values.

Chapter VI presents the study of electric quadrupole interactions in ions arising from electric field gradients due to valence electrons (q_{val}) and crystal field external to ion (q_{lat}). The Sternheimer antishielding factors R and χ_{∞} for q_{val} and q_{lat} respectively are

calculated using the method of direct solution of inhomogeneous Schrödinger equation for the perturbation of the wave functions. The HFS wave functions are used as the unperturbed ones. Due to certain limitations of the method of solution of the Schrodinger equation employed here, the resulting γ_{∞} values are more reliable than the R values. Results of the present calculations on the R values for Pr^{+++} , Tm^{+++} and Ce^{+++} and γ_{∞} values for Na^+ , Cl^- , Al^{+++} , Pr^{+++} , Tm^{+++} , Ce^{+++} , Y^{+++} , In^{+++} , Bi^{+++} and Am^{++} are presented and compared with those of other workers.

A summary of the work reported in this part of the thesis is also presented at the end. This part of the thesis contains 41 Tables and 5 Figures which appear at the appropriate places.

Part B: Saturation in Multilevel-Multiresonance Zeeman Systems: A Theoretical Study

This part of the thesis concerns with a theoretical study of the problem of saturation in multilevel-multiresonance Zeeman systems through the rate equation approach. It comprises of three Chapters and an Appendix.

Chapter I presents a brief description of the multilevel nature of the Zeeman systems and their study through the saturation phenomenon. The rate equation method for obtaining the steady-state population distribution in such systems is discussed and the various approaches to the solution of the rate equations are outlined. Limitation of the rate equation approach is mentioned and it is pointed out that most of the work presented in this part of the thesis was completed prior to the publication of Freed's work (J. Chem. Phys., 43, 2312 (1965)), which does not have the

limitation inherent in the rate equation approach. However, in view of the simplified nature of the present generalization of the application of the rate equation approach to the study of saturation in multilevel-multiresonance Zeeman systems, the present work is believed to have reasonable merit.

In Chapter II, it is shown that the rate equation approaches of Stephen and Fraenkel (the "Diagram Method") and Keating and Barker (the "Inspection Method") are equivalent. This equivalence has not been pointed out earlier in the literature. The "Inspection Method", which was originally formulated for obtaining normalised finite-temperature steady-state population distributions in multilevel-multiresonance Zeeman systems, is extended to develop a general procedure for readily evaluating the various saturation parameters in such systems. The finite temperature case is considered in detail and general expressions for the saturation parameters derived. Expressions in high temperature and infinite temperature cases are deduced from the finite temperature case and compared with those of Stephen. As an illustration, results of some typical calculations are given for a four-level system. Towards the end of Chapter II an expression for the m_I dependence of the saturation parameter Ω for the various hyperfine components in the electron spin resonance spectra of free radicals in dilute solution is obtained. Here, it is assumed that the anisotropic intramolecular electron-nuclear dipole-dipole interaction and g-anisotropy modulation are only the significant relaxation mechanisms present. This m_I dependence seems to be directly verified by the experiments of Schreurs and Fraenkel. Further, it is shown that the expression obtained by Stephen and Fraenkel for the m_I dependence of Ω is a particular form of the expression derived here.

A part of the work reported in this chapter was presented in a Magnetic Resonance Summer School³. It is felt that the simplified rules of the inspection method and the analysis of the saturation factor presented in this chapter can be easily adopted for machine computations.

In Chapter III the inspection method is further extended to take into account the forms of the various lattice-induced relaxation probabilities. In particular, it is assumed here that the various lattice-induced relaxation probabilities are known as linear combinations of certain relaxation parameters, which characterize the relaxation mechanisms present in the system. The present formalism for the study of saturation in multilevel-multiresonance systems has been found to be satisfactory for computer programming of the otherwise rather tedious calculations. The salient features of the FORTRAN computer program written for this purpose are discussed and results of calculation on a six-level and a ten-level system are presented as examples. The computer program appears in the Appendix where a set of sample data and the corresponding output are also presented. Such computations are hoped to be of considerable help in the investigation of the relaxation processes present in multilevel systems. Further, the present computational machinery can be used to evaluate other system parameters which require the knowledge of the steady-state population distribution. A part of the work presented in this chapter is being published shortly⁴.

This part of the thesis contains 13 Tables and 5 Figures which have been inserted at appropriate places. A summary of this part of the thesis appears at its end.

1. "Hartree-Fock-Slater Wave Functions and Magnetic Properties of Rare Gas Atoms".
J. Chem. Phys., 42, 4304 (1965).
2. "Hartree-Fock-Slater Wave Functions and Magnetic Properties of Atoms and Ions".
To appear shortly in "International Journal of Quantum Chemistry", Vol. 1, 1967.
3. "Calculation of Saturation Parameters in Multilevel Zeeman Systems".
Magnetic Resonance Summer School held at Nainital, India (May 1965).
4. "Machine Computation of Saturation Parameters in a Multilevel Zeeman System".
To appear shortly in "Journal of the Franklin Institute", 1967.

TABLE OF CONTENTS

	Page
DEDICATION	i
CERTIFICATE	ii
ACKNOWLEDGEMENT	iii
PREFACE	v

PART A

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND MAGNETIC PROPERTIES OF ATOMS AND IONS

CHAPTER	I	Introduction	1
CHAPTER	II	Hartree-Fock-Slater Wave Functions and Magnetic Properties of Rare Gas Atoms	27
CHAPTER	III	Hartree-Fock-Slater Wave Functions and Magnetic Properties of Atoms and Ions	48
CHAPTER	IV	Fermi-Contact Interaction and Hartree-Fock-Slater Wave Functions	96
CHAPTER	V	Hartree-Fock-Slater Wave Functions and Diamagnetic Susceptibility and Nuclear Magnetic Shielding Values for Neutral Atoms having Open-Shell Configurations	112
CHAPTER	VI	Hartree-Fock-Slater Wave Functions and Quadrupole Antishielding Factors of Atoms and Ions	130
APPENDIX	A		A1
SUMMARY			xv

PART B

SATURATION IN MULTILEVEL-MULTIRESONANCE ZEEMAN SYSTEMS: A THEORETICAL STUDY

CHAPTER	I	Introduction	187
---------	---	--------------	-----

CHAPTER	II	Saturation Parameters in Multilevel- Multiresonance Zeeman Systems	205
CHAPTER	III	Machine Computation of Saturation Parameters in Multilevel-Multiresonance Zeeman Systems	242
APPENDIX	B		B1
SUMMARY			xxiii
VITAE			xxvi.

PART A

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND
MAGNETIC PROPERTIES OF ATOMS AND IONS

CHAPTER I
INTRODUCTION

CHAPTER I

INTRODUCTION

Considerable effort has been made, especially in recent years, to obtain accurate electronic wave functions for many-electron atomic systems. The wave functions are of importance not only from the point of view of the electronic energies but also from the point of view of their ability to predict other physical observables such as dipole and quadrupole polarizabilities, magnetic shielding etc. The latter quantities provide a more stringent test of the wave functions.

The problem of the solution of the Schrodinger equation for a many-electron atomic system was treated notably by Hartree and coworkers¹⁻³. The method was extended with the inclusion of exchange by Fock⁴ and this resulted in the now well-known Hartree-Fock procedure^{2,3}. The solution of the Hartree-Fock equations for a many-electron system is complicated since a large number of exchange integrals have to be evaluated. With the advent of the modern high-speed digital computer facilities it has been

possible to reduce the labour and time considerably and increase the accuracy in the computations without much difficulty. However, if one wishes to obtain the Hartree-Fock functions (HF) for many-electron atomic systems with large atomic number Z the time taken to obtain such solutions increases considerably even with fairly fast computers. Thus it has been pointed out by Lenander⁵ that approximately one hundred hours would be required on IBM 7090 computer to obtain the complete HF solution for a system with Z around 90.

Slater⁶ suggested a method of approximating the exchange potential in the Hartree-Fock equations which reduces the labour and time considerably. Slater's approximation is based on the free-electron gas model. This method was first employed by Pratt⁷ for obtaining Slater-modified Hartree-Fock (SHF) solution for Cu^+ . Herman and Skillman⁸ have been able to obtain wave functions for all neutral atoms in the periodic table by employing Slater's simplified form of the exchange potential and a modification of this potential at large distances from the nucleus. An extensive tabulation of these Hartree-Fock-Slater (HFS) wave functions have been presented by Herman and Skillman along with the details of the computer program in their book⁸. Availability of the HFS wave functions for all neutral atoms and several ions has thus been made possible for the first time. Since the HFS electronic energies compare favourably with available data of HF energies, one is encouraged to test the ability of the HFS wave functions to reproduce other physical observables. Such a test would provide an opportunity to evaluate the merits and demerits of the procedure adopted by Herman and Skillman in evaluating the HFS wave functions. In as much as the HFS method is

attractively simple, such a study would be worthwhile.

This part of the thesis is concerned with such a test of these HFS wave functions with regard to those properties which require the evaluation of expectation values of one-electron operators. In particular, the physical properties chosen are nuclear magnetic shielding (σ), diamagnetic susceptibility (χ), Fermi-Contact interaction term (a_c , the hyperfine splitting constant) and Sternheimer antishielding factors (V_{∞} and R). It may be noted here that the one-electron operators corresponding to σ , χ and V_{∞} and R are $(1/r)$, (r^2) and $(1/(r^3))$ respectively whereas the hyperfine splitting constant a_c is proportional to the value $|\psi(0)|^2$ for the corresponding unpaired s-electron of the system. Thus the present choice of the physical properties provides the test both over small r values and large r values. The degree of accuracy of these physical quantities evaluated using HFS wave functions can be judged by comparing them with the experimental values and the values evaluated using other type of wave functions (e.g. Hartree (H), HF, unrestricted HF (UHF), projected UHF (PUHF), analytic HF etc.) wherever available.

I.1 HARTREE AND HARTREE-FOCK METHODS FOR MANY-ELECTRON ATOMIC SYSTEMS

The nonrelativistic Schrödinger equation for an atomic system containing N electrons is² (in atomic units)

$$\left[-\frac{1}{2} \nabla_j^2 - \sum_j \frac{N}{r_j} + \sum_{i < j} \frac{1}{r_{ij}} \right] \Phi = E \Phi \quad (1.1)$$

This is a non-separable differential equation in $3N$ independent variables and hence needs a simplification for its practical treatment.

In Hartree's self-consistent field method² the approximate solution Ψ_H of the above equation is assumed to be given by the following product of the N one-electron wave functions (orbitals) $\psi_u, \psi_v, \dots, \psi_z$ which are occupied by the various electrons of the system.

$$\Psi_H = \psi_u(1) \psi_v(2) \dots \psi_z(N) \quad (1.2)$$

In other words, this approximation assumes that each electron moves in a field due to the nucleus as well as other electrons. $|\psi_z(N)|^2$ gives the averaged charge density due to N -th electron occupying the z -th orbital. Thus each electron will be moving in the potential of the nucleus and that produced due to charge densities of the rest of the electrons and hence each one of the orbitals can be determined by solving a one-particle Schrodinger equation for the electron concerned in the field of the nucleus and the total averaged charge distribution due to the rest of the electrons which occupy other orbitals. One can thus start with a trial set of functions $\psi_u, \psi_v, \dots, \psi_z$ and make them self-consistent with regard to the field produced by them. The Hartree equations can be derived⁹ using the variational principle of quantum mechanics. Thus, using the form (1.2) of Ψ_H one gets the following Hartree equation¹⁰ for the one-electron wave function ψ_u ,

$$-\frac{1}{2} \nabla_1^2 \psi_u(1) - \frac{N}{r_1} \psi_u(1) + \left[\sum_v \int \psi_v^*(2) \frac{1}{r_{12}} \psi_v(2) d\tau_2 \right] \psi_u(1) - \left[\int \psi_u^*(2) \frac{1}{r_{12}} \psi_u(2) d\tau_2 \right] \psi_u(1) = \lambda_{uu} \psi_u(1) \quad (1.3)$$

Here the summation over v implies summation over all one-electron wave functions including that over u -th one-electron wave function.

The last two terms on the left hand side of equation (1.3) together represent the potential energy of the rest of the electrons distributed in the orbitals other than ψ_u . These are spherically averaged in Hartree's procedure.

In atomic systems the form of one-electron wave functions can be chosen to be that of the central-field type. The most general central-field one-electron wave function occupied by an electron with quantum numbers n , l , m_l and m_s can be written as

$$\psi_u(r_i, \theta_i, \phi_i) = \frac{P_{n,l,m_l,m_s}(r_i)}{r_i} Y_{l,m_l}(\theta_i, \phi_i) S(m_{s_u}) \quad (1.4)$$

This form can be made more restrictive by removing the requirement that $P(r_i)$ in this does depend on m_l , or m_s or on both. However, in the representation

$$\psi_u(r_i, \theta_i, \phi_i) = \frac{P_{nl}(r_i)}{r_i} Y_{l,m_l}(\theta_i, \phi_i) S(m_{s_u}) \quad (1.5)$$

there are $(2l+1)$ spherical harmonics Y 's and two spin functions S . Hence in such a restrictive case $2(2l+1)$ electrons can have the same radial dependence $P_{nl}(r_i)$.

It can be seen that Hartree's product function Ψ_H does not satisfy the antisymmetry principle of Pauli according to which the wave function must be an antisymmetric function of the electron coordinates. In the simplest form an appropriate function Ψ which satisfies the

antisymmetry requirement would be a determinant of the one-electron wave functions such as

$$\Psi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_u(1) & \psi_u(2) & \dots & \psi_u(N) \\ \psi_v(1) & \psi_v(2) & \dots & \psi_v(N) \\ \vdots & \vdots & & \vdots \\ \psi_z(1) & \psi_z(2) & \dots & \psi_z(N) \end{vmatrix} \quad (1.6)$$

It may be noted here that this wave function Ψ allows an electron to occupy any one of the one-electron wave functions $\psi_u, \psi_v, \dots, \psi_z$.

The most simple form of the Hartree-Fock method utilizes the above determinantal form of Ψ . Using variation principle one can derive the following Hartree-Fock equation¹⁰ for the one-electron wave function ψ_u occupied by an electron having spin quantum number $m_{s_u} = m_{s_{\alpha}}$.

$$\begin{aligned} & -\frac{1}{2} \nabla_1^2 \psi_u(1) - \frac{N}{r_1} \psi_u(1) + \left[\sum_v \int \psi_v^*(2) \frac{1}{r_{12}} \psi_v(2) d\tau_2 \right] \psi_u(1) \\ & - \sum_v \delta(m_{s_u} = m_{s_{\alpha}}, m_{s_v}) \left[\int \psi_v^*(2) \frac{1}{r_{12}} \psi_u(2) d\tau_2 \right] \psi_v(1) \\ & = - \sum_v \lambda_{uv} \delta(m_{s_u} = m_{s_{\alpha}}, m_{s_v}) \psi_v(1) \end{aligned} \quad (1.7)$$

The summations over v imply summations over all one-electron wave functions including that over the u -th one-electron wave function.

It can be shown² that the determinantal form (1.6) of Ψ will be adequate for systems having all (nl) groups completely filled (closed-shell configurations) but not so for systems having incomplete (nl) groups (open-shell configurations). In the latter case a linear combination of the determinants of the form (1.6) such as

$$\Psi = \sum_k c_k \Psi_k \quad (1.8)$$

may be used. The form of the HF equations in such a case would not be as simple as the one given above (eqn. 1.7). We need not, however, go into the details of the HF equations obtained using the function Ψ given in equation (1.8).

In the HF equations given earlier (eqn. 1.7) the last term on the left hand side is the well-known exchange term. The important difference between the Hartree (eqn. 1.3) and Hartree-Fock (eqn. 1.7) equations is then the inclusion of the exchange in the latter. The existence of the non-diagonal λ term on the right hand side of HF equations can be removed by choosing a suitable representation of the one-electron wave functions so that λ becomes diagonal.

Use of the form similar to that given in equation (1.4) for one-electron wave functions offers a simplification of the H and HF equations since then the integrations and differentiations over the spherical polar angles can be carried out formally, thus reducing the problem to that of finding the radial functions only. In particular the form (1.5) gives the smallest number of equations.

As far as the solutions of these equations are concerned there are two approaches, namely, Hartree's numerical approach² and the analytic

method of Roothaan¹¹. Lowdin and Appel¹² have suggested a method of analytic fitting to the numerical functions by successive approximations.

For open-shell configurations, the numerical approach has been extended by Brown¹³, Shortley¹⁴ and Hartree^{2,15} while the analytic approach has been extended by Roothaan¹⁶, Huzinaga¹⁷, Roothaan and Bagus¹⁸ and others¹⁹.

As is well-known, relativistic corrections become significant for higher Z systems. Mention may be made here of the work done on relativistic self-consistent field formalisms, for example, by Swirles²⁰, Brown²¹, Mayers²², Cohen²³, Grant²⁴, Synek²⁵, Malli and Roothaan²⁶ and Clementi²⁷.

It is quite obvious that the solution of HF equations is much more complicated than the Hartree equations because of the exchange potential term in the former. Thus, for the higher Z values even with the aid of modern fast digital computers the complete solution of HF equations is formidable. It may be remarked here that although the non-relativistic Hartree solutions are available for quite a large number of systems it is not so with the non-relativistic Hartree-Fock solutions. The number of HF (even non-relativistic) solutions forms only a small fraction of the number of the neutral atoms and the ions met in physical and chemical applications. Thus a large number of theoretical investigations have been handicapped by the lack of HF or even approximate HF wave functions. Fortunately the work of Herman and Skillman⁸ has changed this situation. It is interesting to note that these authors obtained extensive results on atomic wave functions not purely from an interest in atomic structure calculations but in order to make energy band calculations in solids using

these wave functions. We shall deal about the approximation for the exchange term employed by these workers a little later. It would be worthwhile to highlight some of the attempts made recently to get wave functions which are more accurate than the HF functions.

Although HF calculations can be carried out to a high degree of accuracy it has been generally found that the difference between calculated and experimental energy values is significant. This difference, often referred to as the "correlation energy", has its origin in the correlation of the motion of electrons. In Hartree's model no correlation is taken into account whereas in the Hartree-Fock model the correlation between the electrons of like spins is introduced through the use of the determinantal wave function Ψ . It however, neglects the correlation between electrons of unlike spins. There have been several approaches²⁸⁻³¹ to the problem of getting better approximations which include the correlation between unlike spins as well, such as the method of configuration interaction (CI), the method of using correlated wave functions (this cannot work within the framework of HF model) and the method of using different orbitals for different spins (extended HF, unrestricted HF (UHF) and projected UHF (PUHF)).

I.2 THE EXCHANGE TERM IN THE HARTREE-FOCK EQUATIONS AND SLATER'S APPROXIMATION

We shall now focus our attention on the free-electron exchange approximation suggested by Slater⁶ to avoid the evaluation of various exchange integrals in the HF method and thus cast the HF equations in a form suitable for expediting their solution.

The exchange term in the HF equation (eqn. 1.7) can be written as

$$\text{exchange term} = \left[\frac{\sum_v \delta(m_{s_u} = m_{s_\alpha}, m_{s_v}) \int \psi_u^*(1) \psi_v^*(2) \frac{1}{r_{12}} \psi_u(2) \psi_v(1) d\tau_2}{\psi_u^*(1) \psi_u(1)} \right] \psi_u(1) \quad (1.9)$$

The third term on the left hand side of equation 1.7 (HF equation) includes the term $v = u$ which is erroneous as it accounts for the interaction of the electron occupying the orbital ψ_u with itself. The exchange term actually provides a correction for this. Looking at the form (1.9) of the exchange term it can be thought of as being the potential energy of the electron (spin $m_{s_u} = m_{s_\alpha}$) occupying the one-electron wave function ψ_u (at position 1) due to a fictitious charge density at position 2, which one usually refers to as exchange charge density.

exchange charge density

$$= \sum_v \delta(m_{s_u} = m_{s_\alpha}, m_{s_v}) \left[\frac{\psi_u^*(1) \psi_v^*(2) \psi_v(1) \psi_u(2)}{\psi_u^*(1) \psi_u(1)} \right] \quad (1.10)$$

This charge density has the following properties¹⁰.

- (i) Its total amount is 1 a.u. or zero according as ψ_u is occupied or unoccupied.
- (ii) It is made up of only those electrons which have spin m_{s_α} .
- (iii) If position 2 becomes same as position 1 it reduces to total charge density due to electrons having spin m_{s_α} at the position of the electron in question.

The third term on the left hand side of equation (1.7) (HF equation) can be split into two parts, the first including all the electrons having spin $m_{s\beta}$ (opposite to $m_{s\alpha}$) and the second term having all the electrons having spin $m_{s\alpha}$.

First part of the third term on left hand side of equation 1.7
(HF equation)

$$= \sum_v \delta(m_{s\beta}, m_{s_v}) \left[\int \psi_v^*(2) \frac{1}{r_{12}} \psi_v(2) d\tau_2 \right] \psi_u(1) \quad (1.11a)$$

Second part of the third term on left hand side of equation 1.7
(HF equation)

$$= \sum_v \delta(m_{s_u} = m_{s\alpha}, m_{s_v}) \left[\int \psi_v^*(2) \frac{1}{r_{12}} \psi_v(2) d\tau_2 \right] \psi_u(1) \quad (1.11b)$$

If one is considering the one-electron wave function ψ_u for the case when it is actually not occupied, the exchange term will be zero and the third term needs no correction for the self-interaction. However, in case the one-electron wave function ψ_u is occupied, the second part of the third term (eqn. (1.11b)) should contain all the electrons having spin $m_{s\alpha}$ except the one which is occupying the one-electron wave function ψ_u . In this situation a part of the exchange term provides a correction to the third term (actually to second part of the third term) for the self-interaction error.

In case electron position 2 becomes same as position 1 the second part of the third term as a whole becomes meaningless because the

electrons having spin $m_{s\alpha}$ should avoid the electron in question (Pauli's exclusion principle). In this situation the exchange term as a whole provides a correction to the third term on left hand side of equation (1.7); actually cancels out the second part (eqn. 1.11b) of this third term. It may be noted here that in Hartree's model there is a correction for the self-interaction of the electron in question but no correction as regards to operation of Pauli's exclusion principle.

Thus, physically the existence of the charge density in the Hartree-Fock case symbolizes the existence of an exchange-hole centered around the electron in question which keeps the other electrons of the same spin away from it. This hole is also referred to as "Fermi-hole".

In details the exchange charge density and therefore exchange potential have different forms for different occupied one-electron wave functions but they have certain attributes common to all one-electron wave functions. Total exchange charge is 1 a.u. for all ψ 's and when electron position 2 becomes identical with position 1 it is same for all ψ 's and has the maximum value there. Thus one can conclude that the approximate size of the Fermi-holes corresponding to various ψ 's is same though they may have differences in shapes and finer details. One can therefore think of replacing all Fermi-holes by an average value. Assuming that the exchange charge distribution is spherical we can get the radius R of the Fermi-hole from the equation

$$\frac{4}{3} R^3 \rho = 1 \quad (1.12)$$

where ρ represents the exchange charge density which is made up of all electrons having spin $m_{s\alpha}$.

The calculation of average exchange charge density and average exchange potential can be carried out exactly for a free-electron gas^{32,33}. The exchange-hole in a free-electron gas is similar to the exchange-hole in an atomic system in many respects. By analogy with the free-electron gas the averaged exchange potential for an atomic system may be assumed to depend upon local like-spin electronic charge density. Now, to get the value of this averaged exchange potential from the theory of free-electron gas one has to assume that the averaged exchange potential for a non-uniform distribution of electrons as in atomic systems depends only on local electronic charge density. This is the free-electron exchange approximation.

The exchange potential energy for an electron (spin $m_{s\alpha}$) occupying the orbital ψ_u is given in the square bracket of equation (1.9). In the case of free-electron gas this is found out by using the plane wave representation for the various ψ 's so that

$$\psi_v(N) = \frac{1}{\sqrt{V}} e^{+i\vec{K}_v \cdot \vec{r}_N} \quad (1.13)$$

where \vec{K}_v is the wave vector and \vec{r}_N is the radius vector of the N-th electron and V is the volume of the electron gas. Thus the plane wave exchange potential for the electron having the one-electron wave function ψ_u is given by

$$= - \frac{\sum_v \delta(m_{s_u} = m_{s\alpha}, m_{s_v}) \int \frac{1}{r_{12}} \frac{1}{V^2} e^{i(\vec{K}_u - \vec{K}_v) \cdot (\vec{r}_2 - \vec{r}_1)} d\tau_2}{(1/V)} \quad (1.14)$$

Following Dirac-Slater derivation, one first integrates over configuration ($d\tau_2$) and gets the exchange potential energy between electron occupying ψ_u at position 1 and the electron occupying ψ_v . Summation over v implies the integration over momentum space (\vec{K}_v) and this is the second step in Dirac-Slater derivation. One finally gets the momentum (\vec{K}_u)-dependent exchange potential $V_{ex}^{K_u}(r)$ between electron 1 in ψ_u and electrons 2 (m_{s_v} 's = m_{s_u}) in ψ_v 's. Thus, we get

$$V_{ex}^{K_u}(r) = - \frac{2K_{max}(r)}{\pi} \left[\frac{1}{2} + \left\{ \frac{1 - \frac{K_u}{K_{max}(r)}}{4 \frac{K_u}{K_{max}(r)}} \right\}^2 \ln \left\{ \frac{1 + \frac{K_u}{K_{max}(r)}}{1 - \frac{K_u}{K_{max}(r)}} \right\} \right] \quad (1.15)$$

where K_u^2 is the electron energy in atomic units and K_{max}^2 is the Fermi energy. This expression has to be averaged for getting the average exchange potential.

Slater's⁶ averaging emphasizes the interaction with the average electron in the Fermi distribution and he has derived the following expression for the average exchange potential V_{av}^{exch} in the free-electron gas

$$V_{av}^{exch.} = - 3 \left(\frac{3}{8\pi} |\rho| \right)^{\frac{1}{3}} \quad (1.16)$$

where $|\rho|$ represents the total electronic charge density in the free-electron gas.

Now adopting the free-electron exchange approximation the averaged exchange potential in the atomic system at the point r would be equal to the averaged exchange potential for a free-electron gas whose total electronic charge density is equal to that in the atomic system.

Thus replacing $|p|$ in the above equation by $\sum_v \psi_v^*(1) \psi_v(1)$ we get

$$V_{av.}^{exch.}(r) = -3 \left[\frac{3}{8\pi} \sum_v \psi_v^*(1) \psi_v(1) \right]^{\frac{1}{3}} \quad (1.17)$$

Thus, in the free-electron exchange approximation the HF equation (eqn. 1.7) reduces to

$$\begin{aligned} -\frac{1}{2} \nabla_1^2 \psi_u(1) - \frac{N}{r_1} \psi_u(1) + \left[\sum_v \int \psi_v^*(2) \frac{1}{r_{12}} \psi_v(2) d\tau_2 \right] \psi_u(1) \\ - 3 \left[\frac{3}{8\pi} \sum_v \psi_v^*(1) \psi_v(1) \right]^{\frac{1}{3}} \psi_u(1) = \lambda_{uu} \psi_u(1) \end{aligned} \quad (1.18)$$

It has, however, been assumed in the above equation that λ is diagonal. The problem of evaluating the various exchange integrals can be thus avoided. It has been shown, however, that the use of this approximation overemphasizes the role of exchange^{34,35}. Further Maslen's work³⁶, while it tends to support the use of the free-electron exchange approximation in the interior region of an atom, however, points out the serious limitation of this approximation in the exterior region.

1.3 HARTREE-FOCK-SLATER SCHEME OF HERMAN AND SKILLMAN

Herman and Skillman⁸, in their work, have made use of the Slater free-electron exchange potential along with certain other simplifying assumptions. In the first place these workers made use of the representation (1.5) for the orbital ψ_u 's so that they did not distinguish between P_{nlms_α} and P_{nlms_β} . They have also ignored the

multiplet structure arising from the open-shell configurations so as to be able to use the single determinantal form (1.6) of Ψ for all the atoms. For an open-shell configuration all the (nl) orbitals do not have same number of α and β spins so that the free-electron exchange potential for the two sets of spins would not be same. This needs actually a representation which distinguishes between $P_{nlms\alpha}$ and $P_{nlms\beta}$. Using such a representation Pratt³⁷ and Wood and Pratt³⁸ have extended Slater's work to take into account different free-electron exchange potentials for the two sets of spins. These workers, however, have also limited themselves to the use of the single determinantal form of Ψ .

In the representation of Herman and Skillman⁸ the Hartree-Fock-Slater radial equations for a free atom or ion are of the form:

$$-\left[\frac{1}{2} \frac{d^2}{dr^2} + \frac{1(1+1)}{2r^2} + V(r) \right] P_{nl}(r) = E_{nl} P_{nl}(r) \quad (1.19)$$

where distances are measured in Bohr units and energies in Hartree units.

In this equation ordinarily, one has

$$V(r) = V_N(r) + V_{ec}(r) + V_{av}^{exch.}(r) \quad (1.20)$$

where

$$\begin{aligned} V_N(r) &= \text{Nuclear Coulomb potential} \\ &= -\frac{Z}{r} \end{aligned} \quad (1.21a)$$

$$\begin{aligned} V_{ec}(r) &= \text{Total electronic Coulomb potential} \\ &= +\frac{1}{r} \int_0^r \left[\sum_{nl} \omega_{nl} \left\{ P_{nl}(t) \right\}^2 \right] dt + \int_r^\infty \left[\sum_{nl} \omega_{nl} \left\{ P_{nl}(t) \right\}^2 \right] \frac{dt}{t} \end{aligned} \quad (1.21b)$$

and

$$\begin{aligned}
 V_{\text{av.}}^{\text{exch.}}(r) &= \text{Slater average exchange potential} \\
 &= -3 \left[\left(\frac{3}{8\pi} \right) \frac{\omega_{nl} \left\{ P_{nl}(r) \right\}^2}{4\pi r^2} \right]^{\frac{1}{3}}
 \end{aligned}
 \tag{1.21c}$$

ω_{nl} represents the number of electrons (both spins) in the (nl) orbital.

Since at large distances the averaged exchange potential $V_{\text{av.}}^{\text{exch.}}(r)$ goes to zero, it can easily be seen that $V(r) \rightarrow 0$ at such distances for neutral atoms, which is not correct. This shows the existence of self-interaction for an electron at large distances in neutral atoms. We have seen earlier how the self-coulomb potential is removed out of the total electronic coulomb potential by its cancellation with a suitable term in the exchange potential in the HF model. However, because of the fact that the averaged exchange potential goes to zero at large distances, the free-electron exchange approximation fails to cancel the self-coulomb potential at such large distances. In his SHF scheme for the solution of Cu^+ Pratt⁷ did not try to correct for this.

Herman and Skillman⁸ have employed a procedure to "create" the free-electron exchange potential at large distances. In a neutral atom, an electron at large distances must move in the field of a single $(Z-N+1)$ positive charge so that we must have $V(r) = (1/r)$ rather than $V(r) = 0$ at such distances. Herman and Skillman followed Latter's³⁹ procedure for this purpose. The potential $V(r)$ defined by equation (1.20) will now be denoted by $V_0(r)$ and referred to as the unmodified potential. In an atomic system with atomic number Z having N electrons, an electron at large distance would see the potential $-(Z-N+1)/r$. Hence, Herman and Skillman

first choose a critical radius $r=r_0$ given by

$$-\frac{(Z-N+1)}{r} = V_0(r) \quad (1.22)$$

and then define their modified potential $V(r)$ to be used in equation (1.19) as follows

$$\begin{aligned} V(r) &= V_0(r) && \text{for } r < r_0 \\ \text{and } V(r) &= -\frac{(Z-N+1)}{r} && \text{for } r \geq r_0 \end{aligned} \quad (1.23)$$

In spite of the questionable behaviour of $V(r)$ at intermediate r values and the discontinuity in $\frac{dV(r)}{dr}$ at $r=r_0$, these workers have stated that the modified potential $V(r)$ is better than the unmodified potential $V_0(r)$.

The solution obtained by these workers are referred to as HFS wave functions. It may be also pointed out here that the use of the modified potential lowers the energy eigenvalues in general. But the innermost wave functions and their corresponding energy eigenvalues are practically insensitive to the replacement of $V_0(r)$ by $V(r)$. The outermost orbitals are only slightly affected while the corresponding eigenvalues are appreciably lowered. It also turns out that the free-electron exchange approximation fails to correct for the self-coulomb potential at small r values too. Herman and Skillman, however, did not try to correct the potential for this.

It may be remarked here that Herman and Skillman have provided non-relativistic HFS wave functions only. For higher Z atoms the relativistic corrections become important. These workers, however, have calculated the relativistic and spin orbit coupling corrections to various

orbital energy values by a perturbation method. The direct solution of the two first-order linear differential equations resulting from the Dirac relativistic equation in the HFS scheme has been discussed recently by Waber et al.⁴⁰⁻⁴², who have pointed out the improvement resulting from inclusion of relativistic effects also.

I.4 RECENT DEVELOPMENTS OF THE HARTREE-FOCK-SLATER SCHEME

In recent years there have been several developments regarding the Slater free-electron exchange approximation and these will be now discussed.

Following the suggestion of Hartree³⁴, in order to avoid the overemphasis of the role of the exchange in Slater free-electron exchange approximation (SHF), Lenander⁴³⁻⁴⁵ has developed a parameterized Slater-modified Hartree-Fock (PSHF) scheme. This consists of introducing an empirical multiplicative factor in the average exchange potential (eqn. 1.21c).

$$V_{av.}^{exch.,p} = C \left[-3 \left\{ \frac{3}{32 \pi^2 r^2} \sum_{nl} \omega_{nl} \left(P_{nl}(r) \right)^2 \right\}^{\frac{1}{3}} \right] \quad (1.24)$$

In particular, Lenander applied the scheme to Pr^{+++} and obtained the best agreement with HF results for the matrix elements F^2 , F^4 , F^6 (Slater integrals) and $\langle r^2 \rangle$, $\langle r^4 \rangle$ and $\langle r^6 \rangle$ with a value of $C = 4/5$. This factor has also been shown to apply for lower Z atoms or ions such as Cu^+ , O and Ar^{45} .

Kohn and Sham⁴⁶ have arrived at expressions for the exchange potential and correlation based on the earlier work of Hohenberg and Kohn⁴⁷.

APPENDIX B

[illegible]

These authors⁴⁶ obtain the statistical averaged exchange potential which is $2/3$ that of Slater's result (eqn. 1.16). This is because these workers have emphasized the contribution of the electrons at the top of the Fermi distribution while taking the average of $V_{\text{ex.}}^{K_u}(r)$ (see equation 1.15) over K_u . It may be remarked here that Cowan et al.⁴⁸ have also obtained independently this factor $2/3$ in the exchange potential and their derivation also differs somewhat from that of Slater. These latter workers present comparison of wave functions and expectation values of the one electron operators r^n for argon using H, HF, HFS and HFS' (the one which uses an averaged exchange potential which is $2/3$ that of Slater) schemes. They have shown on the basis of their calculations on Ar that HFS' generally yields better results. Tong and Sham⁴⁹ have also discussed the use of the "reduced" exchange potential and correlation corrections outlined by Kohn and Sham⁴⁶ in atomic structure calculations. It may be noted here that both Cowan et al. and Tong and Sham have found it undesirable to use the modification of Herman and Skillman for the exchange potential for large r values in the HFS' scheme.

Lindgren⁵⁰ has recently pointed out an improved Hartree-Fock-Slater method for atomic structure calculations. His method consists of introducing three adjustable parameters C , n and m in the Slater average exchange potential (eqn. 1.21c) as follows.

$$r V_{\text{ex.}}^{\text{imp.}}(r) = C \left[-3 \left\{ \frac{3}{32\pi^2} \right\}^{\frac{1}{3}} (r^{\frac{1}{3}})^n \left\{ \left(\sum_{nl} \omega_{nl} p_{nl}^2(r) \right)^{\frac{1}{3}} \right\}^m \right] \quad (1.25)$$

[illegible]

In the SHF scheme all the parameters C , n and m are equal to unity. Lindgren adjusted these parameters for minimization of total energy and found that while m was fixed constant equal to unity in the three systems studied (Al, K and Cu) C varied from 0.72 to 0.85 and n from 1.01 to 1.24. It can be seen that the value of C is close to the factor $4/5$ obtained by Lenander⁴³. While it is clear that a justification for a C value lower than unity can be obtained from the details of the averaging⁴⁶ of the momentum-dependent exchange potential (eqn. 1.15) it is perhaps rather difficult to justify on physical grounds the introduction of the parameter n . Slater⁵¹ has recently commented on the above proposal for a reduction in the averaged exchange potential. He is of the opinion that the emphasis placed by Kohn and Sham on the electrons near the top of the Fermi distribution is not justified on account of the fact that the dependence of the exchange on the momentum is not experimentally observed and also is practically removed by the plasmon theory of Pines et al.⁵². On this basis Slater prefers to disregard the dependence of the exchange potential on momentum and retain his original form of the averaged exchange potential. The question of reduced Slater exchange potential is still an open one.

I.5 PRESENT WORK

In the work reported in this part of the thesis use has been made of the HFS wave functions obtained with the Slater form of the exchange potential along with ^{the} Herman-Skillman modification.

In view of the fact that the single-determinantal forms of the HFS wave functions are good for closed-shell systems, calculations of

[illegible]

diamagnetic susceptibility (χ_{HFS}) and nuclear-magnetic shielding constant (σ_{HFS}) for all the rare gas atoms have been made and presented in Chapter II. A comparison with available theoretical and experimental data is also made.

In an attempt to test the HFS wave functions also for ions having closed-shell configurations χ_{HFS} and σ_{HFS} values were calculated for the following six isoelectronic series: He, Li^+ , Be^{++} , B^{+++} ; F^- , Ne, Na^+ , Mg^{++} , Al^{+++} ; Cl^- , Ar, K^+ , Ca^{++} , Sc^{+++} ; Br^- , Kr, Rb^+ , Sr^{++} , Yt^{+++} ; I^- , Xe, Cs^+ , Ba^{++} , La^{+++} ; At^- , Rn, Fr^+ , Ra^{++} , Ac^{+++} . The results obtained are reported in Chapter III where our calculations are compared with those of others wherever available. Using the general trends of σ_{HFS} values reported here, an empirical relation has been obtained and used to extrapolate the σ_{HFS} values of atoms and singly, doubly and triply charged positive and negative ions from $Z = 2$ to $Z = 100$. The values thus extrapolated compare reasonably well with those obtained by direct calculation using HFS wave functions. Chapter III also considers an alternative method of evaluating σ_{HFS} values of various isoelectronic series. The method is based on the concept of stability⁵³ of self-consistent field wave functions under one-electron perturbations and requires the knowledge of the total energy values in the isoelectronic series. Since the total HFS energies are not available readily, the method has been demonstrated in an appendix where σ_{HF} values for neutral atoms and singly, doubly and triply charged negative and positive ions in the various isoelectronic series (containing 2 to 27 electrons) have been evaluated using this method. Use is made of HF energy values reported by Clementi⁵⁴, in his work on analytic HF wave functions of

B.2 A SAMPLE DATA

In the following is presented a sample data set which corresponds to the case of a four-level system. This system is similar to the one discussed in section 5 of Chapter II. This level system consists of a single nucleus ($I = \frac{1}{2}$) interacting with an odd-electron ($S = \frac{1}{2}$). The precise labelling of the four-levels which have been assumed is given in the data. The system contains six relaxations and two pumps.

several atoms and ions. The σ_{HF} values thus obtained are compared with those obtained by direct calculation using HF wave functions.

Chapters IV and V are devoted to the study of the HFS wave functions for open-shell configurations. Chapter IV concerns with the calculation of Fermi-Contact interaction terms for some atoms and ions using the HFS wave functions for the s-orbitals corresponding to unpaired electron in each of them. The results are compared with the experimental data, wherever available.

In Chapter V, the results of calculations of χ_{HFS} and σ_{HFS} values for some open-shell configurations in three different regions of the periodic table, namely, $Z = 3$ to $Z = 15$, $Z = 45$ to $Z = 53$ and $Z = 81$ to $Z = 90$ are presented.

Chapter VI presents a study of quadrupole interactions in ions, arising from electric-field gradients due to valence electron (q_{val}) and crystal fields external to the ion (q_{ext}). The contribution to Sternheimer antishielding factors to both q_{val} (R-factor for Pr^{+++} , Ce^{+++} and Tm^{+++}) and q_{ext} (γ_{∞} -factor for Na^+ , Cl^- , Pr^{+++} , Ce^{+++} , Tm^{+++} , Y^{+++} , In^{+++} , Bi^{+++} , Am^{++} and Al^{+++}) are calculated using the method of direct solution of the inhomogeneous Schrodinger equation for the perturbed wave functions. The HFS wave functions are used as unperturbed wave functions. The results are compared with those of other workers.

The discussion of the results obtained here is presented in the individual Chapters and a summary of this part of the thesis appears at the end of it.

REFERENCES

1. D.R. Hartree, Proc. Cambridge Phil. Soc., 24, 89, 111 (1928).
2. D.R. Hartree, "The Calculations of Atomic Structures", John Wiley & Sons, Inc., New York (1957).
3. J.C. Slater, "Quantum Theory of Atomic Structure " Vol. I and II, McGraw Hill Book Co., Inc., New York (1960).
4. V. Fock, Z. Physik, 61, 126 (1930); 62, 795 (1930); 81, 195 (1933).
5. C.J. Lenander, Phys. Rev., 130, 1033 (1963).
6. J.C. Slater, Phys. Rev., 81, 385 (1951).
7. G.W. Pratt, Jr., Phys. Rev., 88, 1217 (1952).
8. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Inc., Englewood Cliffs, New Jersey (1963).
9. J.C. Slater, Phys. Rev., 35, 210 (1930).
10. Ref. 3, Vol. II, Chapter 17.
11. C.C.J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).
12. P.O. Lowdin and K. Appel, Phys. Rev., 103, 1746 (1956).
13. F.W. Brown, Phys. Rev., 44, 214 (1933).
14. G.H. Shortley, Phys. Rev., 50, 1072 (1936).
15. D.R. Hartree and W. Hartree, Proc. Roy. Soc. (London), A150, 9 (1935); A154, 588 (1936).
16. C.C.J. Roothaan, Rev. Mod. Phys., 32, 179 (1960).
17. S. Huzinaga, Phys. Rev., 120, 866 (1960).
18. C.C.J. Roothaan and P. Bagus, "Methods in Computational Physics", Vol. II, Academic Press, Inc., New York (1963).
19. See for example, L.M. Sachs, "A Theoretical Study of Simple Many-Electron Systems", Argonne National Laboratory Report ANL-6310 (1961); S. Huzinaga, Phys. Rev., 122, 131 (1961); F.W. Birss and S. Fraga, J. Chem. Phys., 38, 2552 (1963); S. Fraga, Theoret. Chim. Acta (Berlin), 2, 403 (1964); S. Fraga and F.W. Birss, J. Chem. Phys., 40, 3207 (1964); S. Fraga, Cand. J. Phys., 44, 303, 307 (1966).

VARIGUS TERMS IN
THE POLYNOMIALS
ARE OF THE
FOLLOWING TYPE

1 0 0
1-K L M
0 1 0
2-K L M
0 0 1
3-K L M

WHEN PUMP/PUMPS PRESENT IS/ARE 304, 102,

ALLOWED COMBINATIONS= 4
DISALLOWED COMBINATIONS= 0

INFINITE TEMPERATURE CASE

NUMERATOR FOR OMEGA=

1 0.49999920E 01
3 0.20000000E 01

20. B. Swirles, Proc. Roy. Soc. (London), A152, 625 (1935); A157, 680 (1936).
21. G.E. Brown, Phil. Mag., 43, 467 (1952).
22. D.F. Mayers, Proc. Roy. Soc. (London), A241, 93 (1957).
23. S. Cohen, Phys. Rev., 118, 489 (1960).
24. I.P. Grant, Proc. Roy. Soc. (London), A262, 555 (1961).
25. M. Synek, Phys. Rev., 136, A1552 (1964).
26. G. Malli and C.G.J. Roothaan, Bull. Am. Phys. Soc., 9, 101 (1964).
27. E. Clementi, IBM J. Res. Develop., 9, 2 (1965).
28. P.O. Lowdin in "Advances in Chemical Physics", Ed., I. Prigogine, Interscience Publishers, New York (1959) Vol.II, p. 207.
29. O. Sinanoglu in "Advances in Chemical Physics", Ed., I. Prigogine, Interscience Publishers, New York (1964) Vol. VI, p. 315.
30. O. Sinanoglu and D.F. Tuan, Ann. Rev. Phys. Chem., 15, 251 (1964).
31. "Modern Quantum Chemistry", Istanbul Lectures, Edited by O. Sinanoglu, Part II, Academic Press, New York (1965).
- 31a. R.K. Nesbet in "Advances in Chemical Physics", Ed., I. Prigogine, Interscience Publishers, New York (1965) Vol. IX, p. 321.
32. See ref. 3, Vol. II, Appendix 22.
33. S. Raimes, "The wave Mechanics of Electrons in Metals", Interscience Publishers, Inc., New York (1961).
34. Ref. 2 p. 60.
35. D.R. Hartree, Phys. Rev., 109, 840 (1958).
36. V.W. Maslen, Proc. Phys. Soc. (London), A69, 734 (1956).
37. G.W. Pratt, Jr., Phys. Rev., 102, 1303 (1956).
38. J.H. Wood and G.W. Pratt, Jr., Phys. Rev., 107, 995 (1957).
39. R. Latter, Phys. Rev., 99, 510 (1955); See also C.A. Coulson and C.S. Sharma, Proc. Phys. Soc. (London), 79, 920 (1962).
40. E.C. Snow, J.M. Canfield and J.T. Waber, Phys. Rev., 135, A969 (1964).
41. D. Liberman, J.T. Waber and D.T. Cromer, Phys. Rev., 137, A27 (1965).

42. J.T. Waber and D.T. Cromer, J. Chem. Phys., 42, 4116 (1965).
43. C.J. Lenander, Phys. Rev., 130, 1033 (1963).
44. C.J. Lenander and E.Y. Wong, J. Chem. Phys., 38, 2750 (1963).
45. C.J. Lenander, to be published (Private Communication).
46. W. Kohn and L.J. Sham, Phys. Rev., 140, A1133 (1965).
47. P. Hohenberg and W. Kohn, Phys. Rev., 136, 864 (1964).
48. R.D. Cowan, A.C. Larson, D. Liberman, J.B. Mann and J. Waber, Phys. Rev., 144, 5 (1966).
49. B.Y. Tong and L.J. Sham, Phys. Rev., 144, 1 (1966).
50. I. Lindgren, Arkiv Fysik., 31, 59 (1966).
51. J.C. Slater, Bull. Am. Phys. Soc., 11, 511 (1966).
52. D. Pines, "The Quantum Mechanics of Many-Body Systems", Academic Press, New York (1961).
53. G.G. Hall, Phil. Mag., 6, 249 (1960).
54. See ref. 27 and the extended supplement to this paper, entitled "Tables of Atomic Wave Functions".

CHAPTER II

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND MAGNETIC PROPERTIES OF RARE GAS ATOMS

CHAPTER II

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND MAGNETIC PROPERTIES OF RARE GAS ATOMS*

II.1 INTRODUCTION

In this chapter we present the calculations of diamagnetic susceptibility (χ) and nuclear magnetic shielding constant (σ) for all the rare gas atoms using Hartree-Fock-Slater (HFS) wave functions of Herman and Skillman¹. Although the HFS wave functions for all neutral atoms are available, the closed shell configurations are likely to be more accurately represented by the single determinantal form and hence we have first investigated the rare gas atoms. Section 2 presents the theoretical details of the quantum mechanical calculation of χ and σ values using wave functions. In Section 3 we present details of the numerical evaluation of these quantities. Section 4 presents the results of these calculations and compares them with other available calculations and

* A part of the material presented in this Chapter has been published in J. Chem. Phys., 42, 4304 (1965).

experimental data. In conclusion it is pointed out that the HFS functions appear to be capable of reproducing χ and G value to a good degree of accuracy for rare gas atoms.

II.2 THEORETICAL DETAILS

All atomic and molecular systems show diamagnetism and the atomic diamagnetic susceptibility χ can be computed in a simple manner using the corresponding wave function in the expression²

$$\chi_d = - \frac{e^2}{6mc^2} N \left\langle \Phi \sum_{i=1}^n |r_i|^2 | \Phi \right\rangle \quad (2.1)$$

Here N is Avogadro's number, e is the electronic charge, m is the mass of the electron, c is the velocity of light, r_i is the distance of the i -th electron from the nucleus and Φ is the electronic wave function of the atomic system containing the n electrons. Since Φ is a single determinantal wave function consisting of spin orbitals which are orthonormal, we have

$$\chi_d = - \frac{e^2}{6mc^2} N \sum_{i=1}^n \left\langle P_i(r) | r_i^2 | P_i(r) \right\rangle \quad (2.2)$$

where $P_i(r)$ represents r times the radial part of the spin orbital ψ_i corresponding to i -th electron. Further, in view of the fact that each (nl) group of electrons is characterized by a single spin orbital and it contains $2(2l + 1)$ electrons if it is complete or lesser number of electrons if it is incomplete, we can replace the summation over i by summation over the (nl) spin orbitals as follows

$$\chi_d = - \frac{e^2}{6mc^2} N \sum_{nl} \omega_{nl} \langle P_{nl}(r) | r^2 | P_{nl}(r) \rangle \quad (2.3)$$

where ω_{nl} represents the number of electrons in the (nl) group and

$$n = \sum_{nl} \omega_{nl} \quad (2.4)$$

We have used equation (2.3) to evaluate χ_{HFS} values for the various atoms employing HFS wave functions.

In the molecular beam experiments of Kusch and his coworkers³⁻⁵ it was found necessary to consider the effect of the Larmor precession of electrons in atoms put in a uniform external magnetic field H while attempting to evaluate correctly the magnetic moment of the atomic nucleus. This correction is large especially for heavy atoms. The Larmor precession actually produces a magnetic field at the nucleus which opposes (diamagnetic shielding) the external magnetic field. It has been shown by Kusch et al.³ that \bar{H} , the field due to a single precessing electron at the site of the nucleus in an atom is given by

$$\bar{H} = \frac{e^2 H}{3mc^2} \left\{ 1 / \langle \bar{r} \rangle \right\} \quad (2.5)$$

where \bar{r} is the mean value of the distance of the electron from the nucleus and e , m and c represent the same physical quantities as those in equation (2.1). Lamb⁶ showed that the shielding field is directly proportional to the electrostatic potential produced by the electrons at the nucleus. Further, using Thomas-Fermi Model he derived the relation

$$10^5 \frac{\bar{H}}{H} = C(Z)^{\frac{4}{3}} \quad (2.6)$$

for the ratio of the shielding field to the external field. Here $C = 0.319 \times 10^{-4}$ and Z is the nuclear charge.

Following Lamb⁶, Hylleraas and Skavlem⁷ also derived the formula

$$-\frac{\bar{H}}{H} = \frac{1}{3} \alpha^2 \left\langle \frac{a_H}{r} \right\rangle_{av}. \quad (2.7)$$

where a_H is the Bohr radius and α is the fine structure constant.

It may be noted that following the derivations of Lamb⁶ and Dickenson⁸, for an atom or monoatomic ion in a magnetic field H , there will be an induced shielding $H'(0)$ at the nucleus such that

$$\frac{H'(0)}{H} = \frac{e^2}{3mc^2} v(0) \quad (2.8)$$

where $v(0)$ is the electrostatic potential produced by the electrons at the nucleus.

Since in the self-consistent field method the spherical symmetry of the potential is assumed at the outset, we can calculate $v(0)$ simply using the appropriate atomic wave function and thus

$$\sigma = \frac{e^2}{3mc^2} \left\langle \Phi \left| \sum_{i=1}^n \left(\frac{1}{r_i} \right) \right| \Phi \right\rangle \quad (2.9)$$

We shall consider here only the diamagnetic part of the shielding of the nucleus due to the electronic precession. Contributions to the shielding from orbital and spin parts are not considered here. Although the above equations apply strictly speaking to atoms and ions in $1S$ state the diamagnetic part of the nuclear shielding in atoms and ions

having states other than 1S can be calculated by the above equation and the values thus obtained pertain to the spherically averaged values $\overline{\sigma} = \frac{1}{3}(\overline{\sigma}_{xx} + \overline{\sigma}_{yy} + \overline{\sigma}_{zz})$.

Following the same reasoning as used in deriving equation (2.3) from equation (2.1) we can get here also a relation quite similar to (2.3) for evaluating $\overline{\sigma}$ quantum mechanically. Thus we have

$$\overline{\sigma} = \frac{e^2}{3mc^2} \sum_{nl} \omega_{nl} \left\langle P_{nl}(r) \left| \frac{1}{r} \right| P_{nl}(r) \right\rangle \quad (2.10)$$

In the following section we describe the procedure in which the relations (2.3) and (2.10) are used to evaluate χ and $\overline{\sigma}$ for rare gas atoms using the relevant spin-orbitals.

II.3 METHOD OF CALCULATION

For evaluating χ_{HFS} and $\overline{\sigma}_{\text{HFS}}$ values of an atom or ion we require $\langle P_{nl}(r) | r^2 | P_{nl}(r) \rangle$ and $\langle P_{nl}(r) | (1/r) | P_{nl}(r) \rangle$, i.e. expectation values using the various spin-orbitals (nl) of the system. These were evaluated by direct numerical integration using the numerical HFS wave functions of Herman and Skillman on IBM 1620 computer.

The HFS wave functions are available as x vs. $P(x)$ tables. x is the variable appearing in the Thomas-Fermi model of the atom and is defined¹ by

$$x = \frac{r}{\mu} \quad (2.11)$$

where μ is a function of Z , the atomic number and is defined as

$$\mu = \left(\frac{1}{2}\right) \left(\frac{3\pi}{4}\right)^{\frac{2}{3}} (Z)^{-\frac{1}{3}} \quad (2.12)$$

Both x and r are taken in atomic units. In terms of the variable x we have for the k -th orbital,

$$\begin{aligned}
 \langle P_k(r) | r^m | P_k(r) \rangle &= \int_0^\infty P_k(r) r^m P_k(r) dr \\
 &= \int_0^\infty P_k(r=\mu x) \mu^m x^m P_k(r=\mu x) \mu dx \\
 &= (\mu)^{m+1} \int_0^\infty P_k(r=\mu x) x^m P_k(r=\mu x) dx \\
 &= (\mu)^{m+1} \langle P_k(r=\mu x) | x^m | P_k(r=\mu x) \rangle
 \end{aligned}
 \tag{2.13}$$

In particular, we have

$$\langle P_{nl}(r) | r^2 | P_{nl}(r) \rangle = (\mu)^3 \langle P_{nl}(x) | x^2 | P_{nl}(x) \rangle
 \tag{2.14a}$$

$$\text{and } \langle P_{nl}(r) | 1/r | P_{nl}(r) \rangle = \langle P_{nl}(x) | 1/x | P_{nl}(x) \rangle
 \tag{2.14b}$$

We utilized the data of Herman and Skillman in terms of x vs. $P(x)$ tables directly through equations (2.14a) and (2.14b).

The method of finite differences⁹⁻¹² was used in the numerical integration of equations (2.14a) and (2.14b). In particular, the integration formula through adjacent intervals, namely, the formula

$$\begin{aligned}
 f_{j+1} - f_j &= \frac{1}{2}(\delta x) \left[f_j' + f_{j+1}' - \frac{1}{12} (\delta^2 f_j' + \delta^2 f_{j+1}') + \frac{11}{720} (\delta^4 f_j' + \delta^4 f_{j+1}') \right. \\
 &\quad \left. + O(\delta x)^7 \right]
 \end{aligned}
 \tag{2.15}$$

was employed. We actually evaluated the integrals

$$\begin{aligned} \int_0^{\infty} P_{nl}(x) x^m P_{nl}(x) dx &= \int_0^{x_{\infty}^{nl}} P_{nl}(x) x^m P_{nl}(x) dx \\ &= \int_0^{x_{\infty}^{nl}} F_{nl}(x) dx \end{aligned} \quad (2.16)$$

$$\text{where} \quad F_{nl}(x) = P_{nl}(x) x^m P_{nl}(x) \quad (2.17)$$

and x_{∞}^{nl} represents the limiting value of x in the outer region where $P_{nl}(x_{\infty}^{nl})$ is less than certain prescribed minimum. $P_{nl}(x)$ decays exponentially with x and so this cut-off is required and all $P(x)$ beyond x_{∞}^{nl} are set equal to zero. In other words, the contribution to the above type of integrals from $x = x_{\infty}^{nl}$ to $x = \infty$ is neglected. In the tables of ref.1 values of $P(x)$ less than 0.0001 in the decaying region have been set equal to zero.

We have used here the "presentation mesh"¹ of Herman and Skillman as our "integration mesh". This is a 110-point mesh containing various blocks, each of which consists of ten points and corresponds to a characteristic Δx value. The Δx values double themselves as we go from one region to the adjacent outer region. The innermost region corresponds to $\Delta x = 0.01$ a.u.

Formula (2.15) is used for each of the blocks and the integration 2.16 is performed block-wise.

To evaluate the integral $\int_{x=a}^{x=b} F_{nl}(x) dx$ for a block $x = a$ to

$x = b$ we utilize the mesh points of this block. If there are J entries in this block we have

$$\left. \begin{aligned} x_1 &= a \\ x_J &= b \\ \Delta x &= (b-a)/J \end{aligned} \right\} \quad (2.18)$$

From equation (2.15) with $f' = F_{nl}(x)$ we get

$$\begin{aligned} \int_{x=a}^{x=b} F_{nl}(x) dx &= \int_{x=x_1}^{x=x_J} F_{nl}(x) dx \\ &= (f_J - f_1) = (f_2 - f_1) + (f_3 - f_2) + (f_4 - f_3) + \dots + (f_J - f_{J-1}) \\ &= \frac{1}{2}(\Delta x) \left[\sum_{j=1}^J \left\{ F_{nl}(x_{j+1}) + F_{nl}(x_j) \right\} - \frac{1}{12} \sum_{j=1}^J \left\{ \delta^2 F_{nl}(x_{j+1}) + \delta^2 F_{nl}(x_j) \right\} \right. \\ &\quad \left. + \frac{11}{720} \sum_{j=1}^J \left\{ \delta^4 F_{nl}(x_{j+1}) + \delta^4 F_{nl}(x_j) \right\} \right] \end{aligned} \quad (2.19)$$

It is obvious from this equation that in order to include differences upto fourth it is necessary to have two extra entries at both the boundaries of the block. Hence, for this purpose, each block is first properly overlapped with its two adjacent blocks before the integrals are evaluated for each of them. Finally, the net integral (2.16) is obtained by summing the contributions from the various blocks.

Utilizing the values of the integrals (2.16) for $m = 2$ and $m = -1$ for the various spin-orbitals of the atom in equations (2.3) and (2.10) through equations (2.14) we finally calculate χ_{HFS} and σ_{HFS} values for the atom.

A FORTRAN computer program has been written for this purpose. It takes the desired atomic wave functions one by one and calculates the corresponding χ_{HFS} and G_{HFS} values. It also provides necessary and useful intermediate results such as $\langle r^2 \rangle_{nl}$ and $\langle (1/r) \rangle_{nl}$ integral for each orbital, contributions from each block of a given orbital and contributions to the integrals from the second difference term, as well as from the fourth difference term in each block of a given orbital. In a single run the program can handle data for several atomic systems.

II.4 RESULTS AND DISCUSSION

The diamagnetic susceptibility values and nuclear magnetic shielding constants of the rare gas atoms calculated using 110-point HFS wave functions of ref. 1 are given in Tables II.1 and II.2 respectively. These tables also compare the present calculations with other calculations using Hartree (H) or Hartree-Fock (HF) wave functions¹³⁻²⁶.

Roothaan and Weiss²⁷ calculated the susceptibility of He using correlated wave functions of both closed-shell and open-shell type and their results are not very different from the value -1.887×10^{-6} cgs emu/mole. The experimental value chosen by these authors for comparison is that of Wills and Hector²⁸ who obtained a value -1.88×10^{-6} cgs emu/mole. The recent measurements of susceptibility of He by Barter et al.²⁹ have, however, yielded a value of $-2.02 \pm 0.08 \times 10^{-6}$ cgs emu/mole. The difference between χ_{HF} and $\chi_{\text{exptl.}}$ values for He is more than the uncertainty quoted in the measurement of Barter et al. Our χ_{HFS} value for He is in good agreement with that of Barter et al. The agreement between χ_{HFS} values and the experimental data for neon, argon

TABLE II.1

HFS Diamagnetic Susceptibility (χ_{HFS}) Values for Rare Gas Atoms
(All Values in -1×10^6 cgs emu/mole units)

Atom	χ_{HFS} (Present Work)	$\chi^{(a)}$ $\chi_{\text{exptl.}}$	$\chi_{\text{H/HF}}$ (Previous Work)
He	1.95	2.02 ± 0.08	1.93^c 1.878^d $1.88-1.89^e$
Ne	7.09	6.96 ± 0.14	7.38^c 7.475^d 7.4^f 5.8^g
Ar	19.17	19.32 (unweighted)	20.626^b 20.90^c
Kr	29.06	29.00 ± 0.40	31.315^b 33.00^c
Xe	43.93^h	45.54 ± 0.70	44.846^b
Rn	59.37		

a) See ref. 29

b) See ref. 30 (using analytic HF wave functions, He, Ne, Ar & Kr- ref. 26, Xe- ref. 25)

c) T.G. Strand and R.A. Bonham, J. Chem. Phys., 40, 1686 (1964) (using analytic expression for $\langle r^n \rangle$ from HF functions; He- ref. 19, Ne- ref. 23, Ar- ref. 21 & Kr- ref. 22)

d) See ref. 38 (using single determinantal analytic SCF-HF functions of Roothaan type; He- ref.18, Ne- ref.20)

e) See ref. 27 (using correlated (closed and open shell) HF function for He)

f) A.Gold and R.S. Knox, Phys. Rev., 113, 834 (1959) (using HF function of ref. 17)

g) K.E. Banyard, J. Chem. Phys., 33, 832 (1960) (using analytic central field wave function with exchange-ref.16)

h) A value of 45.95 has been recently obtained using the 441- point mesh wave functions (K.M.S. Saxena and P.T. Narasimhan, Int. J. Quantum Chem., to be published).

TABLE II.2

HFS Nuclear Magnetic Shielding Values ($\sigma_{\text{HFS}} \times 10^5$) for Rare Gas Atoms

Atom	σ_{HFS} (Present Work)	$\sigma_{\text{H/HP}}$ (Other Calculations)				
He	6.00	5.990 ^a	5.990 ^b	6.00 ^c	5.990 ^d	5.985 ^e 6.002 ^f 5.990 ^g
Ne	56.30	55.226 ^a	55.227 ^b	54.70 ^c	55.241 ^d	55.108 ^e 55.108 ^g
Ar	125.40	123.760 ^a	123.764 ^b	124.00 ^c		124.530 ^g
Kr	327.40	324.559 ^a	234.561 ^b	321.00 ^c		328.740 ^g
Xe	567.80	563.847 ^a	564.232 ^b	559.00 ^c		
Rn	1076.80	1072.00 ^a	1072.820 ^b	1060.00 ^c		

a) See ref. 31 (using analytic HF functions; He, Ne- ref. 26, Ar- his own wave function, Kr- ref. 26 and Rn ref. 25)

b) C. Froese and G. Malli, Slater Symposium, University of Florida, Jan.1967; G. Malli, (Private Communication)

c) See ref. 8 (using H/HP functions; He- ref. 13, Ne- ref. 14, Ar- ref. 15, Kr, Xe and Rn by interpolation)

d) See ref. 38 (using single determinantal analytic SCF-HF functions of Roothaan type; He- ref. 18, Ne- ref. 20).

e) F.O. Ellison, J. Chem. Phys., 40, 2421 (1964); 41, 2018 (1964) (using rescaled functions of ref. 24)

f) M.L. Rustgi and P. Tewari, J. Chem. Phys., 39, 2590 (1963) (using function of ref. 18)

See also footnote d

g) R.A. Bonham and T.G. Strand, J. Chem. Phys., 40, 3447 (1964) (using analytic HF expression for electron density $\langle(r)\rangle$ and $\langle(1/r)\rangle$) (see also ref. 27)

and krypton is also very good. The agreement between our χ_{HFS} values and χ_{HF} values reported by Malli and Fraga³⁰ using analytic HF wave functions is also satisfactory. However, the present $|\chi_{\text{HFS}}|$ value for Xe is less than both the corresponding $|\chi_{\text{exptl.}}|$ and the $|\chi_{\text{HF}}|$ (ref. 29) values by nearly 4% and 2% respectively. It may be pointed out that these differences in the χ_{HFS} value for Xe from the corresponding χ_{HF} and $\chi_{\text{exptl.}}$ values can now be ascribed to the use of a 110-point mesh for the integration.

As we shall see in Chapter III when we use a finer mesh of 441-point the resulting χ_{HFS} value (-45.95×10^{-6} cgs emu/mole) agrees well with χ_{HF} and also with $\chi_{\text{exptl.}}$ values. Further our χ_{HFS} values also agree fairly well with those of Strand and Bonham (see footnote c of Table II.1) for He and Ne. But the difference between our values and theirs increases as we go to Ar and Kr which might indicate that the analytic fit to the HF potential obtained by these workers is not satisfactory for higher Z values.

Calculations for the diamagnetic susceptibility of radon using H or HF wave functions do not appear to have been done so far. The $\chi_{\text{exptl.}}$ value for radon is also not available. On the basis of the excellent agreement with experiment obtained for the χ values for rare gas atoms upto Xe it is believed that the χ_{HFS} value of -59.37×10^{-6} cgs emu/mole for radon reported here is fairly reliable.

It is seen from Table II.2 that, in general, χ_{HFS} values agree best with χ_{HF} values reported by Malli and Fraga³¹ using analytic HF wave functions. In particular, we notice that, for helium χ_{H} , χ_{HF} and χ_{HFS} differ almost negligibly; for neon, argon, krypton and radon χ_{HF} is less than χ_{HFS} . While the agreement between our χ_{HFS} values and χ_{HF} values is quite good for Kr, Xe and Rn it is seen that the values calculated by

Dickinson⁸ by interpolation differ significantly. The accuracy of such interpolated values is not therefore high.

Our σ_{HFS} values are generally slightly higher than other quoted values. Since σ values bear a direct relationship to the potential produced by the electrons of the atomic system at the site of the nucleus we may conclude that HFS wave functions yield a slightly higher value for this potential in comparison to HF wave functions. As pointed out earlier in Chapter I the HFS wave functions of Herman and Skillman¹ have been obtained by modifying the Slater averaged exchange potential in the outer regions ("tail correction") while a correction needed for the inner regions has not been made. It is probable that this feature is responsible for the observed behaviour in the calculated σ_{HFS} values. Additional evidence for this fact is forthcoming from the χ_{HFS} values which agree very well with χ_{HF} and $\chi_{\text{exptl.}}$ values and it may be pointed out that χ values are sensitive to the outer regions of the orbitals.

Tong and Sham³² and Cowan et al.³³ have recently obtained some rare gas atom wave functions using HFS procedure but with an exchange potential which is 2/3 that given by Slater (vide Chapter I). The justification for the use of a reduced Slater exchange potential has been given by Kohn and Sham³⁴ and independently by Cowan et al.³³ Both these groups of workers (ref. 32 and 33) did not find it useful to make the tail correction of Herman and Skillman for the Slater exchange potential. Tong and Sham, who obtained $\sum \langle r^2 \rangle$ values for Ne, Ar and Kr, have also investigated the effect of including correlation in the wave functions following the method of Kohn and Sham³⁴. Cowan et al. have made available $\sum \langle 1/r \rangle$ and $\sum \langle r^2 \rangle$ values for argon only. It is of great interest

to compare the χ and σ values obtained using reduced Slater potential with the σ_{HFS} values obtained in this work and with the σ_{HF} values. We have therefore used the expectation values $\sum \langle 1/r \rangle$ and $\sum \langle r^2 \rangle$ given in references 32 and 33 and calculated χ and σ values. The values obtained using the reduced Slater potential will be referred to as χ_{HFS} , and σ_{HFS} . From the data given by Cowan et al. for Ar we thus find $\sigma_{\text{HFS}} = 123.48 \times 10^{-5}$. This may be compared with σ_{HF} and σ_{HFS} values (vide Table II.2) of 123.76×10^{-5} and 125.40×10^{-5} respectively. It is seen that the use of the reduced potential yields a σ value which is very close to σ_{HF} . If one uses HFS wave functions for argon³³ obtained with unmodified Slater exchange potential (without the tail correction) one obtains a σ value of 125.49×10^{-5} . This clearly indicates that the tail correction does not affect the σ values very much and again confirms our earlier remark on σ_{HFS} and the need for correcting the exchange potential for the inner regions as well in the formalism of Herman and Skillman¹. Multiplying the Slater exchange potential by a constant factor two-thirds as done by Kohn and Sham and other workers yields better agreement for the inner regions as justified by the σ_{HFS} value for argon. The HFS' wave functions thus resemble very closely the HF wave functions in these inner regions. However, a uniform alteration of the exchange potential for all regions does not seem to yield the desired results. This can be seen from the χ_{HFS} values for Ne, Ar and Kr calculated from the data of Tong and Sham³². These χ_{HFS} values are summarized in Table II.3 along with χ_{HF} , χ_{HFS} and $\chi_{\text{exptl.}}$ values. It is seen here that $|\chi_{\text{HFS}}|$ (column 3 of Table II.3) are larger than $|\chi_{\text{HFS}}|$ and $|\chi_{\text{HF}}|$ as well as experimental values. Even approximate inclusion of correlation following the method of

TABLE II.3

Comparison of χ Values for Some Rare Gas Atoms Obtained with and without Reduction of the Slater Exchange Potential
(All Values in -1×10^6 cgs emu/mole Units)

Atom	$\chi_{\text{HFS}}^{(a)}$	$\chi_{\text{HFS}}^{(b)}$		$\chi_{\text{HF}}^{(c)}$	$\chi_{\text{exptl.}}^{(d)}$
		Correlation term not included	Approximate Correlation term included		
Ne	7.09	7.950	7.835	7.429	6.96 ± 0.14
Ar	19.17	21.233^e	20.956	20.626	19.32 (unweighted)
Kr	29.06	31.942	31.559	31.315	29.00 ± 0.40

a) The values of present calculation using HFS wave functions of Herman and Skillman (ref. 1). This adopts Slater exchange potential and its tail correction.

b) The values calculated using $\sum \langle r^2 \rangle_{\text{HFS}}$ data reported by Tong and Sham (ref. 32). This adopts reduced Slater exchange potential by a factor two-thirds (Kohn and Sham, ref. 34) and no tail correction.

c) Values reported by Malli and Fraga (ref. 30).

d) Values reported by Barter et al. (ref. 29); see also Table II.1

e) $\sum \langle r^2 \rangle_{\text{HFS}}$ value for argon reported by Cowan et al. also yields same value (21.233). These authors also used the two-thirds reduced Slater exchange potential with no tail correction.

Kohn and Sham³⁴ does not appear to improve the results much although it somewhat reduces the χ_{HFS} values.

Gowan et al. have quoted $\sum \langle r^2 \rangle$ value for argon using HFS scheme but without the tail correction of Herman and Skillman. The value corresponding to this wave function is -18.477×10^{-6} cgs emu/mole which is much larger than our χ_{HFS} value (-19.17×10^{-6} cgs emu/mole). This clearly indicates the importance of the tail correction for the outer region of the wave functions especially in the HFS scheme. It has been reported³³ that tail correction in the HFS' scheme yields poorer results.

In view of the above discussion it would be of interest to try out two modifications of the HFS scheme in relation to χ and σ value for rare gas atoms. Lenander³⁵⁻³⁷ has proposed an empirical factor 4/5 instead of 2/3 for reducing the Slater exchange potential. One could employ the tail correction of Herman and Skillman along with Lenander's 4/5 factor and compute χ and σ values. Alternatively, one could employ the Herman-Skillman approach but include a correction in the Slater's exchange potential for the inner regions also. To our knowledge, a comparison between such results and HF values as well as experimental values has not yet been made.

Table II.4 gives the values of one-electron $\langle r^2 \rangle_{\text{HFS}}$ and $\langle (1/r) \rangle_{\text{HFS}}$ integrals for the various orbitals of helium and neon. A comparison of these integrals has been made with those of Sidwell and Hurst³⁸ who have reported their values using HF wave functions^{18,20}. The agreement between our results and theirs is satisfactory. $\langle r^2 \rangle_{\text{HFS}}$ and $\langle (1/r) \rangle_{\text{HFS}}$ values for the various orbitals in the other rare gas atoms

TABLE II.4

One Electron $\langle r^2 \rangle_{\text{HFS}}$ and $\langle 1/r \rangle_{\text{HFS}}$ Integrals for He and Ne
(in Atomic Units)

Atom	Orbital	$\langle r^2 \rangle_{\text{HFS}}$ (Present Work)	$\langle r^2 \rangle_{\text{HF}}$ (Ref. 38)	$\langle 1/r \rangle_{\text{HFS}}$ (Present Work)	$\langle 1/r \rangle_{\text{HF}}$ (Ref. 38)
He	1s	1.2336	1.18480	1.6923	1.6873
Ne	1s	0.0331	0.03347	9.6740	9.6178
	2s	0.9380	0.96967	1.6741	1.6321
	2p	1.1680	1.23810	1.5014	1.4364

obtained with 441-point mesh are presented later in Chapter III.

It will be worthwhile to discuss here some aspects of the details of the integrations done here for evaluating various expectation values. As has been pointed out in section 3, beyond the cut-off value of x (i.e. x_{∞}^{nl}) the values of $P_{nl}(x)$ are less than 0.0001 and they have been put equal to zero in the tables of ref. 1. Our experience in using these wave functions shows that this cut-off is not a serious handicap in the calculations since the contributions to the present integrals from the outermost regions are not significant. Although we have included the contributions from the outermost region, it may be pointed out that when the values of x are such that $P_{nl}(x)$ values are less than 0.003, the magnitude of the contributions to the present integrals from such outer regions is so small as to be almost negligible.

The HFS wave functions used here are non-relativistic and are therefore not quite accurate for heavy atoms especially for inner orbitals where the electrons move with speeds comparable to the speed of light. Further, for such atoms the inner orbitals become very much contracted with the result that $P_{nl}(x)$ is a rapidly varying function of x . Since the x values corresponding to various blocks are common for all the orbitals and atoms the entries in the x vs. $P(x)$ tables for these inner orbitals are smaller in number. Consequently, for such orbitals errors in the numerical integration are likely to occur. This can be avoided by the use of smaller Δx values for the various blocks. Use of the 441-point integration mesh of Herman and Skillman¹ would therefore be better. As for as the χ_{HFS} values are concerned, the errors due to use of non-relativistic wave functions will not be much since the contributions

to χ values from the outer orbitals are much more than those from the inner orbitals. On the other hand σ_{HFS} values can be improved especially for heavier systems using relativistic HFS wave functions because the electrons nearest to the nucleus contribute the most to σ values. It may be pointed out here that recently relativistic HFS wave functions have started³⁹ appearing in the literature. No attempt has, however, been made here to use these wave functions.

II.5 CONCLUSION

Since the wave functions of the rare gas atoms can be represented by a single determinant, these systems provide us with an opportunity to evaluate the merits and demerits of the HFS wave functions. The results obtained here with HFS wave functions are very encouraging. It has been shown that the diamagnetic susceptibility values (χ_{HFS}) obtained from HFS wave functions are as good as those obtained from HF wave functions. On the other hand the nuclear magnetic shielding (σ_{HFS}) values are uniformly higher than σ_{HF} . A reduction of the Slater exchange potential appears to improve the results of σ . The need for tail correction in the outer regions of the Slater exchange potential has been pointed out. From a discussion of the available results using reduced Slater exchange potential it is concluded that such a uniform reduction in the exchange potential may not by itself lead to better results. The need for correcting the potential in both the inner and outer regions has been emphasized.

REFERENCES

1. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Inc., Englewood Cliffs, New Jersey (1963).
2. J.H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Clarendon Press, Oxford (1932).
3. P. Kusch, S. Millman and I.I. Rabi, Phys. Rev., 55, 1176 (1939); 57, 765 (1940).
4. P. Kusch and S. Millman, Phys. Rev., 56, 527 (1939).
5. S. Millman and P. Kusch, Phys. Rev., 58, 438 (1940); 60, 91 (1941).
6. W.E. Lamb, Jr., Phys. Rev., 60, 817 (1941).
7. E. Hylleraas and S. Skavlem, Phys. Rev., 79, 117 (1950).
8. W.C. Dickenson, Phys. Rev., 80, 563 (1950).
9. D.R. Hartree, "The Calculation of Atomic Structures", John Wiley and Sons, Inc., New York (1957), Chapter 4.
10. D.R. Hartree, "Numerical Analysis", Oxford (1955).
11. L.M. Milne-Thomson, "Calculus of Finite Differences", Macmillan (1933).
12. F.B. Hildebrand, "Introduction to Numerical Analysis", McGraw Hill Book Co. (1956).
13. D.R. Hartree, Proc. Cambridge Phil. Soc., 24, 111 (1927-1928).
14. F.W. Brown, Phys. Rev., 44, 214 (1933) (with exchange).
15. D.R. Hartree, Proc. Roy. Soc., (London), A166, 450 (1938) (with exchange).
16. C.A. Coulson and W.E. Duncanson, Proc. Roy. Soc. (Edinburg), 62A, 37 (1944).
17. B.H. Worsley, Can. J. Phys., 36, 289 (1958).
18. C.C.J. Roothaan, L.M. Sacks and A. Weiss, Rev. Mod. Phys., 32, 186 (1960).
19. C.C.J. Roothaan, L.M. Sacks and A. Weiss, Rev. Mod. Phys. 32, 191 (1960).
20. L.C. Allen, J. Chem. Phys., 34, 1156 (1961).

21. R.E. Watson and A.J. Freeman, Phys. Rev., 123, 521 (1961).
22. R.E. Watson and A.J. Freeman, Phys. Rev., 124, 1117 (1961).
23. E. Clementi, C.C.J. Roothaan and M. Yoshimine, Phys. Rev., 127, 1618 (1962).
24. F.O. Ellison and N.T. Huff, J. Chem. Phys., 39, 2051 (1963).
25. M. Synek and G.E. Stungis, J. Chem. Phys., 42, 3068 (1965).
26. E. Clementi, IBM J. of Res. and Develop., 9, and the extended supplement to this paper, entitled "Tables of Atomic Wave Functions".
27. C.C.J. Roothaan and A. Weiss, Rev. Mod. Phys., 32, 194 (1960).
28. A.P. Wills and L.G. Hector, Phys. Rev., 23, 209 (1924); 24, 418 (1924).
29. C. Barter, R.G. Meisenheimer and D.F. Stevenson, J. Phys. Chem., 64, 1312 (1960).
30. G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin), 5, 284 (1966).
31. G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin), 5, 275 (1966).
32. B.Y. Tong and L.J. Sham, Phys. Rev., 144, 1 (1966).
33. R.D. Cowan, A.C. Larson, D. Liberman, J.B. Mann and J. Weber, Phys. Rev., 144, 5 (1966).
34. W. Kohn and L.J. Sham, Phys. Rev., 140, A1133 (1965).
35. C.J. Lenander, Phys. Rev., 130, 1033 (1963).
36. C.J. Lenander and E.Y. Wong, J. Chem. Phys., 38, 2750 (1963).
37. C.J. Lenander, to be published (Private Communication).
38. T.W. Sidwell and R.P. Hurst, J. Chem. Phys., 37, 203 (1962).
39. D. Liberman, J.T. Waber and D.T. Cromer, Phys. Rev., 137, A27 (1965).

CHAPTER III

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND MAGNETIC PROPERTIES OF ATOMS AND IONS

CHAPTER III

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND MAGNETIC PROPERTIES OF ATOMS AND IONS*

III.1 INTRODUCTION

In Chapter II it has been shown that diamagnetic susceptibility and nuclear magnetic shielding values of rare gas atoms can be calculated to a good degree of accuracy using Hartree-Fock-Slater wave functions of Herman and Skillman¹. The single determinantal form of the HFS wave functions leads one to expect that these wave functions will be equally well suited for other closed-shell systems. In an attempt to check on the reliability of these wave functions also for ions having closed shell configurations χ_{HFS} and ϵ_{HFS} values were calculated for the following six isoelectronic series: He, Li⁺, Be⁺⁺, B⁺⁺⁺; F⁻, Ne, Na⁺, Mg⁺⁺, Al⁺⁺⁺; Cl⁻, Ar, K⁺, Ca⁺⁺, Sc⁺⁺⁺; Br⁻, Kr, Rb⁺, Sr⁺⁺, Yt⁺⁺⁺; I⁻, Xe, Cs⁺, Ba⁺⁺, La⁺⁺⁺; At⁻, Rn, Fr⁺, Ra⁺⁺, Ac⁺⁺⁺.

* Part of the work presented in this Chapter is due to appear in the International Journal of Quantum Chemistry (1967).

The method of calculation is the same as that adopted in Chapter II. However, there are some additional features of the present calculations such as the use of a finer mesh of 441-point in the numerical integrations. These are discussed in section 2 of this Chapter.

The calculated χ_{HFS} and σ_{HFS} values are reported in section 3 where they are compared with other available calculations and the results are also discussed there. Using the present values of σ_{HFS} for the rare gas atoms the variation of σ_{HFS} with Z , the atomic number, has been expressed as a polynomial and thus shielding values for all neutral atoms with $Z = 2$ to $Z = 100$ could be obtained. The extrapolated values have been checked at points $Z = 6, 14, 27, 45$ and 70 where direct calculations of σ_{HFS} using the wave functions were also made. The σ_{HFS} values of atoms and ions in the above-mentioned isoelectronic series reveal rather interesting trends which could be detected in the present calculations because of the use of a self-consistent set of wave functions (the HFS wave functions) throughout the calculations. For example, in a given isoelectronic series it has been found that as one goes from the neutral rare gas atom to the next singly charged positive isoelectronic ion, the σ_{HFS} value increases by a certain amount, say δ_+ . If now one calculates the σ_{HFS} value for a doubly charged positive isoelectronic ion it turns out that the shielding increases further by almost the same amount, δ_+ as compared to the singly charged positive isoelectronic ion. This feature has been confirmed for all positive ions upto triply charged ones and for all the six isoelectronic series. Further, it has been also found that δ_+ itself varies as one goes from one isoelectronic series to the other. It has also been observed that as one goes from a rare gas atom to the corresponding

isoelectronic singly charged negative ion the shielding value decreases by an amount δ_- and that $\delta_- \approx \delta_+$ for all the rare gas atoms. δ_- is in fact slightly greater than δ_+ in all the six isoelectronic series. Unfortunately, our calculations are limited in this regard only to singly charged negative ions due to the problem of obtaining HFS wave functions for negative ion with charge more than or equal to two. The nature of this problem is discussed in section 2. However, on account of the well-established trend with regard to the positive ions and the fact that $\delta_- \approx \delta_+$ for all rare gas atoms we have been able to obtain a closed empirical relation for extrapolating the σ_{HFS} values for atoms and ions in general. The details of the derivation of this relationship is given in section 3. We have used our expression to extrapolate the σ_{HFS} values for neutral atoms, singly, doubly and triply charged positive and negative ions from $Z = 2$ to $Z = 100$. The values thus extrapolated are compared with those obtained by direct calculation using HFS wave functions.

In section 4 values of the various one electron $\langle r^2 \rangle_{\text{HFS}}$ and $\langle (1/r) \rangle_{\text{HFS}}$ integrals are reported. Some interesting features with regard to the variation of $\langle (1/r) \rangle_{\text{HFS}}$ values with respect to Z , the atomic number; n , the principal quantum number and l , the azimuthal quantum number have been observed. These are also discussed in this section.

Section 5 of this Chapter includes a discussion of an alternative method of evaluating σ_{HFS} values for various isoelectronic series. This method is based on the concept of stability² of SCF wave functions under one-electron perturbations and requires the knowledge of the Z -dependence of the total energy values in the isoelectronic series. Since the total HFS energy values are not available readily, the method has been

demonstrated in an Appendix where σ_{HF} values for neutral atoms and singly, doubly and triply charged positive and negative ions in various isoelectronic series containing two to twentyseven electrons have been evaluated. Use is made of the total HF energy values reported by Clementi³ in his work on analytic HF wave functions of positive ion isoelectronic series including neutral atoms. The σ_{HF} values obtained here seem to be as good as those obtained by direct calculation using these HF wave functions.

III.2 DETAILS OF CALCULATIONS

The theoretical aspects of the quantum-mechanical calculation of χ_{HFS} and σ_{HFS} for the various systems undertaken here are the same as those given in section 2 of Chapter II. The numerical procedure adopted here for evaluation of various one-electron integrals is also the same as that adopted for the calculation of χ_{HFS} and σ_{HFS} values for the rare gas atoms (see Section 3, Chapter II).

In order to achieve greater accuracy in the present work we have used here the 441-point HFS wave functions. As already indicated in section 4 of Chapter II, for fast-varying functions significant errors might result by the use of a smaller size mesh. Thus, it has been found that, whereas most of our earlier results (Chapter II) obtained with 110-point mesh are not significantly altered, with the use of a finer 441-point mesh, a slight discrepancy could be detected in the case of xenon. Here it was observed that the value of the diamagnetic susceptibility calculated with the 110-point mesh was -43.93×10^{-6} cgs emu/mole whereas the value obtained by integration with the 441-point mesh wave function is

77574

demonstrated in an Appendix where σ_{HF} values for neutral atoms and singly, doubly and triply charged positive and negative ions in various isoelectronic series containing two to twentyseven electrons have been evaluated. Use is made of the total HF energy values reported by Clementi³ in his work on analytic HF wave functions of positive ion isoelectronic series including neutral atoms. The σ_{HF} values obtained here seem to be as good as those obtained by direct calculation using these HF wave functions.

III.2 DETAILS OF CALCULATIONS

The theoretical aspects of the quantum-mechanical calculation of χ_{HFS} and σ_{HFS} for the various systems undertaken here are the same as those given in section 2 of Chapter II. The numerical procedure adopted here for evaluation of various one-electron integrals is also the same as that adopted for the calculation of χ_{HFS} and σ_{HFS} values for the rare gas atoms (see Section 3, Chapter II).

In order to achieve greater accuracy in the present work we have used here the 441-point HFS wave functions. As already indicated in section 4 of Chapter II, for fast-varying functions significant errors might result by the use of a smaller size mesh. Thus, it has been found that, whereas most of our earlier results (Chapter II) obtained with 110-point mesh are not significantly altered, with the use of a finer 441-point mesh, a slight discrepancy could be detected in the case of xenon. Here it was observed that the value of the diamagnetic susceptibility calculated with the 110-point mesh was -43.93×10^{-6} cgs emu/mole whereas the value obtained by integration with the 441-point mesh wave function is

77574

demonstrated in an Appendix where σ_{HF} values for neutral atoms and singly, doubly and triply charged positive and negative ions in various isoelectronic series containing two to twentyseven electrons have been evaluated. Use is made of the total HF energy values reported by Clementi³ in his work on analytic HF wave functions of positive ion isoelectronic series including neutral atoms. The σ_{HF} values obtained here seem to be as good as those obtained by direct calculation using these HF wave functions.

III.2 DETAILS OF CALCULATIONS

The theoretical aspects of the quantum-mechanical calculation of χ_{HFS} and σ_{HFS} for the various systems undertaken here are the same as those given in section 2 of Chapter II. The numerical procedure adopted here for evaluation of various one-electron integrals is also the same as that adopted for the calculation of χ_{HFS} and σ_{HFS} values for the rare gas atoms (see Section 3, Chapter II).

In order to achieve greater accuracy in the present work we have used here the 441-point HFS wave functions. As already indicated in section 4 of Chapter II, for fast-varying functions significant errors might result by the use of a smaller size mesh. Thus, it has been found that, whereas most of our earlier results (Chapter II) obtained with 110-point mesh are not significantly altered, with the use of a finer 441-point mesh, a slight discrepancy could be detected in the case of xenon. Here it was observed that the value of the diamagnetic susceptibility calculated with the 110-point mesh was -43.93×10^{-6} cgs emu/mole whereas the value obtained by integration with the 441-point mesh wave function is

-45.948×10^{-6} cgs emu/mole and this latter value is in very good agreement with the experimental value of $-45.54 \pm 0.70 \times 10^{-6}$ cgs emu/mole reported by Barter et al.⁴ Our new value is also in good agreement with the value obtained recently by Malli and Fraga⁵ who used Hartree-Fock analytic wave functions. A comparison of the HFS wave functions on the 110-point and 441-point mesh clearly revealed the nature of the trouble as due to the somewhat inadequate representation in the former case of the functions at regions where it was varying fast. A Herman-Skillman type HFS program¹ was used on IBM 7044 computer at I.I.T., Kanpur to obtain the required wave functions on the 441-point mesh.

It may be pointed out that, while using the Herman-Skillman type HFS program the self consistency criterion¹, $\beta(\text{SCF})$ for the modified HFS potential¹ in the form $rV_o(r)$ was taken to be 0.001. This guarantees that the potential $rV_o(r)$ is self-consistent to at least 1 part in 1000. The eigenvalue accuracy criterion¹ was chosen to be 0.00001. The 110-point mesh wave functions used by us in our earlier work (Chapter II) were from the book¹ of Herman and Skillman which were reported in an abridged form and their listing terminated towards their exponentially decaying regions when they became less than 0.0001. This is, however, not so with the unabridged 441-point mesh wave functions obtained directly in the present work using a Herman-Skillman type HFS program. This information is available to eight significant figures. Thus in the present work in addition to the fact that the mesh is finer, the entries used have eight significant figures. The unabridged numerical information about the radial wave functions was directly put onto a magnetic tape in an appropriate form which facilitates the use of our susceptibility and shielding computer

program. Thus while preparing this input tape, the various blocks of the 441-point mesh were properly overlapped at their boundaries by suitably modifying the "HFS Wave Functions" program.

As reported in section 1 of this Chapter, our calculations of χ_{HFS} and σ_{HFS} do not include the doubly and triply-charged negative ions. This is due to the problem of obtaining convergence in the "HFS Wave Functions" program which is serious for the case of negatively charged ions. In spite of our several attempts to obtain convergence in the HFS Wave Functions program for doubly and triply charged negative ions we have been unable to obtain it⁶. Even in the case of a singly charged negative ion like F^- we have noted that the convergence problem is quite serious since no convergence could be obtained by us within the usual 40 iterations for this system. We could, however, obtain convergence for F^- after 82 iterations! It seems to us that the problem of obtaining bound states in the Hartree-Fock-Slater model with the addition of electrons to a given atom needs further attention.

III.3 RESULTS AND DISCUSSION: EXTRAPOLATION OF SHIELDING VALUES FOR ATOMS AND IONS BY GENERAL Z-POLYNOMIAL FITTING

The diamagnetic susceptibility values and nuclear magnetic shielding constants of atoms and ions with closed-shell configurations calculated using the 441-point HFS wave functions are given in Tables III.1 and III.2 respectively where results of other calculations^{5,7-20} are also included in footnotes. The agreement is found to be satisfactory, in general. However, it can easily be seen from these tables that just as in the case of rare gas atoms (Chapter II) a slight disagreement creeps in as one goes to higher Z values. This is probably due to relativistic effects,

TABLE III.1

HFS Diamagnetic Susceptibility Values (χ_{HFS}) for Atoms and Ions with Closed-Shell Configurations
(All Values in -1×10^6 cgs emu/mole units)

Isoelectronic Series No.	Ions with Charge -1	χ_{HFS}	Neutral Atoms	χ_{HFS}	Ions with Charge +1	χ_{HFS}	Ions with Charge +2	χ_{HFS}	Ions with Charge +3	χ_{HFS}
1	-	-	He	1.954116 ^c	Li ⁺	.7226212 ^d	Be ⁺⁺	.3736362	B ⁺⁺⁺	.2278033
2	F ⁻	12.79442 ^{a,b}	Ne	7.088091 ^c	Na ⁺	4.842605 ^d	Mg ⁺⁺	3.574414	Al ⁺⁺⁺	2.764167
3	Cl ⁻	28.69906 ^b	Ar	19.16469 ^c	K ⁺	14.46134 ^d	Ca ⁺⁺	11.49084	Sc ⁺⁺⁺	9.426939
4	Br ⁻	39.61456 ^b	Kr	29.05791 ^c	Rb	23.53449	Sr ⁺⁺	19.84712	Yt ⁺⁺⁺	17.14557
5	I ⁻	58.64890	Xe	45.94762 ^c	Cs ⁺	38.79615	Ba ⁺⁺	33.30470	La ⁺⁺⁺	30.01650
6	At ⁻	73.32141	Rn	59.67446 ^c	Fr ⁺	51.78176	Ra ⁺⁺	46.16339	Ac ⁺⁺⁺	41.82115

- a) Sidwell and Hurst (ref. 7) reported a value 12.70 using analytic HF wave function of Allen (ref. 65).
b) Malli and Fraga (ref. 5) reported values 12.638, 30.335 and 42.204 for F⁻, Cl⁻ and Br⁻ respectively using analytic HF wave functions of Clementi (ref. 3).
c) For comparison of these values with the other available values see Table II.1 in Chapter II.
d) Malli and Fraga (ref. 5) reported values 0.706, 5.078 and 15.472 for Li⁺, Na⁺ and K⁺ respectively using analytic HF wave functions of Clementi (ref. 3).

TABLE III.2

HFS Nuclear Magnetic Shielding Values ($\sigma_{\text{HFS}} \times 10^5$) for Atoms and Ions with Closed-Shell Configurations

Isoelectronic Series No.	Ions with Charge -1	Neutral Atoms	σ_{HFS}	Ions with Charge +1	σ_{HFS}	Ions with Charge +2	σ_{HFS}	Ions with Charge +3	σ_{HFS}
1	-	He	6.007678 ^b	Li ⁺	9.545017 ^{c,f}	Be ⁺⁺	13.08935 ^f	B ⁺⁺⁺	16.63620 ^f
2	F ⁻	Ne	49.05580 ^{a,g}	Na ⁺	63.43422 ^c	Mg ⁺⁺	70.56825	Al ⁺⁺⁺	77.69083
3	Cl ⁻	Ar	116.5672 ^a	K ⁺	134.1614 ^c	Ca ⁺⁺	142.9285	Sc ⁺⁺⁺	151.6577
4	Br ⁻	Kr	315.6592 ^a	Rb ⁺	339.2468 ^e	Sr ⁺⁺	350.9515	Yt ⁺⁺⁺	362.6239
5	I ⁻	Xe	554.5184 ^d	Cs ⁺	581.5168 ^e	Ba ⁺⁺	594.9349	La ⁺⁺⁺	608.3198
6	At ⁻	Rn	1061.946 ^d	Fr ⁺	1094.480 ^e	Ra ⁺⁺	1110.658	Ac ⁺⁺⁺	1126.799

Malli and Fraga (ref. 18) reported values 48.021, 114.930 and 312.719 for F⁻, Cl⁻ and Br⁻ using analytic HF wave functions of Clementi (ref. 3); Sidwell and Hurst (ref. 7) reported a value 48.025 for F⁻ using analytic HF wave function of Allen (ref. 65). For comparison of these values with other available values see Table II.2 in Chapter II. Malli and Fraga (ref. 18) reported values 9.540, 62.238 and 132.540 for Li⁺, Na⁺ and K⁺ respectively using analytic HF wave functions of Clementi (ref. 3). Malli and Fraga (ref. 18) reported extrapolated values 569.483 and 1131.838 for I⁻ and At⁻ respectively by fitting a three parameter formula. Malli and Fraga (ref. 18) reported extrapolated values 334.636, 568.798 and 1045.631 for Rb⁺, Cs⁺ and Fr⁺ respectively by fitting a three parameter formula. Ellison (ref. 15) reported values 9.5298, 13.0774, 16.6193 for Li⁺, Be⁺⁺ and B⁺⁺⁺ respectively using a power series fit to empirical total energy values and a relation between this power series and σ (A discussion of this procedure is given in section 5). Ellison (ref. 15) reported a value 47.9333 for F⁻ (see also the preceding footnote f).

the HFS wave functions used here being non-relativistic. For the case of Li^+ , Tong and Sham²¹ have given $\sum \langle r^2 \rangle_{\text{HFS}}$ value using HFS' wave functions with approximate inclusion of correlation (see Chapter II). Their value corresponds to $\chi_{\text{HFS}} = -0.743 \times 10^{-6}$ cgs emu/mole. It may be noted that this value is even higher than our χ_{HFS} value. Tong and Sham have also given $\sum \langle r^2 \rangle_{\text{HFS}}$ values for Na^+ with and without correlation. The corresponding χ_{HFS} values are -5.239×10^{-6} cgs emu/mole and -5.286×10^{-6} cgs emu/mole. Again it is seen that these values are higher than χ_{HFS} values and that the inclusion of correlation affects the value only slightly. The χ_{HF} values reported by Malli and Fraga⁵ for Li^+ and Na^+ are -0.706×10^{-6} cgs emu/mole and -5.078×10^{-6} cgs emu/mole. The reduction in the Slater exchange potential used in the HFS' scheme does not appear to bring χ_{HFS} values closer to χ_{HF} .

From the values of σ_{HFS} for neutral atoms at the points $Z = 2, 10, 18, 36, 54$ and 86 it is observed that σ_{HFS} increases as one goes to higher and higher Z values. Similar behaviour is true for σ_{H} or σ_{HF} and several workers have tried different formulae to extrapolate the nuclear magnetic shielding values especially for those atoms and ions for which the direct calculation is not possible due to non-availability of the wave functions. For example, Lamb¹⁷ derived the following expression for the nuclear magnetic shielding using Thomas-Fermi-Dirac model of the atom.

$$\sigma(Z) = \left[\frac{(3.19)}{(10^5)} \right] (Z)^{\frac{4}{3}} \quad (3.1)$$

Malli and Fraga¹⁸ extrapolated the nuclear magnetic shielding constants for neutral atoms and singly-charged positive and negative ions

from $Z = 2$ to $Z = 107$ by fitting a three-parameter formula of the type

$$\sigma(Z) = k (Z' - s)^t \quad (3.2)$$

to the values calculated directly using analytic HF wave functions. Here Z' stands for the number of the electrons in the system with atomic number Z and k , s and t are the three parameters.

We have used, however, a general polynomial in Z to extrapolate the nuclear magnetic shielding constants of neutral atoms. Using our values of σ_{HFS} for neutral atoms with $Z = 2, 10, 18, 36, 54$ and 86 (column 5 of Table III.2) we tried to fit a polynomial using the least square technique^{22,23}. A tolerance of 0.1×10^{-1} was specified but it was found that with the limited number of points, namely six, the best possible polynomial was the following fourth-order polynomial with the standard error 0.4×10^{-1} :

$$\sigma_{\text{HFS}}(Z) = (a_0) + (b_0)Z + (c_0)Z^2 + (d_0)Z^3 + (e_0)Z^4 \quad (3.3)$$

where,

$$\left. \begin{aligned} a_0 &= -2.92634 \\ b_0 &= 4.07000 \\ c_0 &= 0.204929 \\ d_0 &= -0.212361 \times 10^{-2} \\ \text{and } e_0 &= 0.103515 \times 10^{-4} \end{aligned} \right\} \quad (3.4)$$

If $A^-(Z-1)$, $B(Z)$, $C^+(Z+1)$, $D^{++}(Z+2)$ and $E^{+++}(Z+3)$ represent an isoelectronic series containing a closed-shell atom B with atomic number Z , it can be easily seen from Table III.2 (each row of which corresponds to an isoelectronic series) that in general, $(\sigma_{C^+} - \sigma_B)$,

$(\sigma_{D++} - \sigma_{C+})$ and $(\sigma_{E+++} - \sigma_{D++})$ are almost equal to each other and are individually slightly lower than $(\sigma_E - \sigma_A)$. This feature of the six isoelectronic series is evident from Table III.3.

Using values of $\delta_+(Z)$ av. at the points $Z = 2, 10, 18, 36, 54$ and 86 (column 7 of Table III.3) and those for $\delta_-(Z)$ at the points $Z = 10, 18, 36, 54$ and 86 (column 3 of Table III.3) we fitted polynomials for them using again the method of least squares with the tolerance 0.1×10^{-1} . Here also we found that with the limited number of points available the best possible polynomials were the following fourth-order polynomials with standard error 0.38 for $\delta_+(Z)$ and negligible for $\delta_-(Z)$:

$$\delta_+(Z) = (a_+) + (b_+)Z + (c_+)Z^2 + (d_+)Z^3 + (e_+)Z^4 \quad (3.5)$$

$$\text{and } \delta_-(Z) = (a_-) + (b_-)Z + (c_-)Z^2 + (d_-)Z^3 + (e_-)Z^4 \quad (3.6)$$

where

$$\left. \begin{aligned} a_+ &= 2.56859 \\ b_+ &= 0.551632 \\ c_+ &= -0.137827 \times 10^{-1} \\ d_+ &= 0.182593 \times 10^{-3} \\ e_+ &= -0.878065 \times 10^{-6} \end{aligned} \right\} \quad (3.7)$$

and

$$\left. \begin{aligned} a_- &= 5.25192 \\ b_- &= 0.182718 \\ c_- &= 0.217841 \times 10^{-2} \\ d_- &= -0.803085 \times 10^{-4} \\ e_- &= 0.554069 \times 10^{-6} \end{aligned} \right\} \quad (3.8)$$

TABLE III.3

Variation of the HFS Nuclear Magnetic Shielding Values ($\sigma_{\text{HFS}} \times 10^5$) in The Various Isoelectronic Series

Isoelectronic Series (A ⁻ , B, C ⁺ , D ⁺⁺ , E ⁺⁺⁺) Number	The Neutral Atom B and its At. No.	$\sigma_+(Z)$					
		$\sigma_B^- \sigma_{A^-}$	$\sigma_{C^+}^- \sigma_B$	$\sigma_{D^{++}}^- \sigma_{C^+}$	$\sigma_{E^{+++}}^- \sigma_{D^{++}}$	Average	
1	He (Z=2)	-	3.537339	3.544333	3.546850	3.542841	
2	Ne (Z=10)	7.221780	7.156640	7.134030	7.122580	7.137750	
3	Ar (Z=18)	8.837300	8.776900	8.747100	8.729200	8.751067	
4	Kr (Z=36)	11.83610	11.75150	11.70470	11.67240	11.70953	
5	Xe (Z=54)	13.53680	13.46160	13.41810	13.38490	13.42153	
6	Rn (Z=86)	16.30500	16.22900	16.17800	16.14100	16.18267	

Although the HFS wave functions obtained are of the single determinantal type the σ results for non-closed shell systems are expected to be fairly reliable since it has been shown¹⁸ that the contributions from states other than ground do not alter the results significantly. Hence, by properly combining the polynomials for $\sigma_{\text{HFS}}(Z)$, $\delta_+(Z)$ and $\delta_-(Z)$, one can write a general extrapolation formula for nuclear magnetic shielding constants. Thus, we have the following formula for $\sigma_{\text{HFS}}^{\pm n}(Z \pm n)$ which is the HFS nuclear magnetic shielding value for an ion having the charge $\pm n$, nuclear charge $Z \pm n$ and being isoelectronic with the neutral atom with atomic number Z :

$$\begin{aligned}
 & \sigma_{\text{HFS}}^{\pm n}(Z \pm n) \\
 &= \sigma_{\text{HFS}}(Z) \pm n \left\{ \delta_{\pm}(Z) \right\} \\
 &= \left\{ (a_0)_{\pm n}(a_{\pm}) \right\} + \left\{ (b_0)_{\pm n}(b_{\pm}) \right\} Z + \left\{ (c_0)_{\pm n}(c_{\pm}) \right\} Z^2 + \left\{ (d_0)_{\pm n}(d_{\pm}) \right\} Z^3 \\
 & \quad + \left\{ (e_0)_{\pm n}(e_{\pm}) \right\} Z^4 \quad (3.9)
 \end{aligned}$$

Note that as n tends to zero, equation (3.9) goes to equation (3.3).

Employing equation (3.9) we have extrapolated the nuclear magnetic shielding constants for neutral atoms ($Z = 2$ to $Z = 100$) and for singly, doubly and triply charged positive and negative ions in the ninety-nine isoelectronic series. These values are listed in Table III.4. In order to check the degree of accuracy of the extrapolation within the frame-work of self-consistency of HFS wave functions we have also directly calculated the nuclear magnetic shielding constants for a few

TABLE III.4

Extrapolated Values of HFS Nuclear Magnetic Shielding ($\sigma_{\text{HFS}} \times 10^5$) for Atoms with $Z=2$ to $Z=100$ and Isoelectronic Ions

Z	For Negative Ions with			For the Neutral		For Positive Ions with		
	Atoms with			Atoms with		Atoms with		
	Charge = -3 At. No. = Z-3	Charge = -2 At. No. = Z-2	Charge = -1 At. No. = Z-1	At. No. Z	Charge = +1 At. No. = Z+1	Charge = +2 At. No. = Z+2	Charge = +3 At. No. = Z+3	
1	2	3	4	5	6	7	8	
2	-	-	-	6.016550	9.634720	13.25289	16.87106	
3	-	-	5.253960	11.07152	15.17582	19.28012	23.38442	
4	-	4.473960	10.48661	16.49926	21.06531	25.63137	30.19743	
5	3.657070	9.867340	16.07762	22.28790	27.29236	32.29681	37.30127	
6	9.195750	15.60577	22.01579	28.42582	33.84632	39.26683	44.68734	
7	15.06721	21.67869	28.29016	34.90163	40.71681	46.53200	52.34718	
8	21.26152	28.07576	34.88999	41.70422	47.89367	54.08311	60.27255	
9	27.76894	34.78686	41.80479	48.82271	55.36694	61.91117	68.45539	
10	34.57994	41.80211	49.02429	56.24646	63.12691	70.00736	76.88782	
11	41.68522	49.11184	56.53847	63.96510	71.16411	78.36312	85.56213	
12	49.07565	56.70660	64.33754	71.96848	79.46926	86.97004	94.47082	

Table III.4 (Continued)

1	2	3	4	5	6	7	8
13	56.74236	64.57715	72.41194	80.24673	88.03334	95.81995	103.6066
14	64.67664	72.71450	80.75236	88.79022	96.84755	104.9049	112.9622
15	72.87002	81.10986	89.34970	97.58954	105.9033	114.2171	122.5308
16	81.31423	89.75468	98.19513	106.6356	115.1923	123.7489	132.3056
17	90.00119	98.64060	107.2800	115.9194	124.7063	133.4932	142.2800
18	98.92305	107.7595	116.5960	125.4324	134.4375	143.4426	152.4476
19	108.0722	117.1035	126.1349	135.1662	144.5782	153.5902	162.8022
20	117.4411	126.6650	135.8888	145.1126	154.5210	163.9294	173.3378
21	127.0227	136.4364	145.8501	155.2638	164.8587	174.4536	184.0485
22	136.8098	146.4105	156.0113	165.6120	175.3842	185.1565	194.9287
23	146.7957	156.5804	166.3652	176.1499	186.0909	196.0318	205.9728
24	156.9737	166.9392	176.9048	186.8704	196.9721	207.0739	217.1757
25	167.3375	177.4805	187.6235	197.7664	208.0217	218.2769	228.5321
26	177.8808	188.1977	198.5146	208.8315	219.2334	229.6353	240.0372
27	188.5978	199.0849	209.5720	220.0591	230.6015	241.1439	251.6863
28	199.4826	210.1361	220.7896	231.4431	242.1203	252.7976	263.4748

Table III.4 (Continued)

1	2	3	4	5	6	7	8
210.5296	221.3456	232.1616	242.9776	253.7845	264.5914	275.3983	
221.7335	232.7080	243.6825	254.6570	265.5889	276.5208	287.4527	
233.0892	244.2181	255.3469	266.4758	277.5285	288.5812	299.6340	
244.5918	255.8708	267.1498	278.4288	289.5987	300.7685	311.9383	
256.2364	267.6614	279.0863	290.5112	301.7948	313.0785	324.3621	
268.0187	279.5852	291.1518	302.7183	314.1128	325.5073	336.9019	
279.9342	291.6380	303.3418	315.0456	326.5486	338.0515	349.5544	
291.9788	303.8156	315.6523	327.4890	339.0983	350.3075	362.3167	
304.1488	316.1141	328.0794	340.0446	351.7583	363.4720	375.1857	
316.4404	328.5298	340.6193	352.7087	364.5254	376.3422	388.1589	
328.8500	341.0593	353.2686	365.4778	377.3965	389.3151	401.2337	
341.3746	353.6993	366.0241	378.3489	390.3685	402.3882	414.4078	
354.0109	366.4469	378.8829	391.3188	403.4389	415.5590	427.6791	
366.7562	379.2992	391.8421	404.3851	416.6053	428.8254	441.0455	
379.6077	392.2536	404.8994	417.5452	429.8653	442.1853	454.5054	
392.5632	405.3078	418.0524	430.7970	443.2170	455.6371	468.0571	

able III.4 (Continued)

1	2	3	4	5	6	7	8
45	405.6203	418.4597	431.2991	444.1385	456.6588	469.1790	481.6992
46	418.7770	431.7074	444.6377	457.5681	470.1889	482.1098	495.4306
47	432.0315	445.0491	458.0667	471.0843	483.8063	496.5282	509.4502
48	445.3823	458.4835	471.5871	484.6859	497.5096	510.3334	523.1572
49	458.8279	472.0092	485.1906	498.3719	511.2982	524.2245	537.1509
50	472.3671	485.6254	498.8836	512.1418	525.1714	538.2011	551.2308
51	485.9991	499.3310	512.6630	525.9950	539.1288	552.2627	565.3966
52	499.7229	513.1257	526.5285	539.9313	553.1703	566.4093	579.6483
53	513.5381	527.0090	540.4800	553.9509	567.2959	580.6409	593.9859
54	527.4443	540.9809	554.5174	568.0539	581.5058	594.9578	608.4097
55	541.4414	555.0413	568.6411	582.2410	595.8007	609.3605	622.9202
56	555.5294	569.1906	582.8517	596.5129	610.1813	623.8496	637.5180
57	569.7087	583.4294	597.1500	610.8707	624.6484	638.4261	652.2039
58	583.9796	597.7583	611.5370	625.3157	639.2034	653.0911	666.9789
59	598.3430	612.1785	626.0140	639.8495	653.8477	667.8459	681.8442
60	612.7996	626.6910	640.5824	654.4737	668.5829	682.6921	696.8012

able III.4 (Continued)

1	2	3	4	5	6	7	8
45	405.6203	418.4597	431.2991	444.1385	456.6588	469.1790	481.6992
46	418.7770	431.7074	444.6377	457.5681	470.1889	482.1098	495.4306
47	432.0315	445.0491	458.0667	471.0843	483.8063	496.5282	509.4502
48	445.3823	458.4835	471.5871	484.6859	497.5096	510.3334	523.1572
49	458.8279	472.0092	485.1906	498.3719	511.2982	524.2245	537.1509
50	472.3671	485.6254	498.8836	512.1418	525.1714	538.2011	551.2308
51	485.9991	499.3310	512.6630	525.9950	539.1288	552.2627	565.3966
52	499.7229	513.1257	526.5285	539.9313	553.1703	566.4093	579.6483
53	513.5381	527.0090	540.4800	553.9509	567.2959	580.6409	593.9859
54	527.4443	540.9809	554.5174	568.0539	581.5058	594.9578	608.4097
55	541.4414	555.0413	568.6411	582.2410	595.8007	609.3605	622.9202
56	555.5294	569.1906	582.8517	596.5129	610.1813	623.8496	637.5180
57	569.7087	583.4294	597.1500	610.8707	624.6484	638.4261	652.2039
58	583.9796	597.7583	611.5370	625.3157	639.2034	653.0911	666.9789
59	598.3430	612.1785	626.0140	639.8495	653.8477	667.8459	681.8442
60	612.7996	626.6910	640.5824	654.4737	668.5829	682.6921	696.8012

Table III.4 (Continued)

1	2	3	4	5	6	7	8
61	627.3506	641.2973	655.2439	669.1905	683.4108	697.6311	711.8514
62	641.9975	655.9991	670.0007	684.0022	698.3338	712.6653	726.9968
63	656.7415	670.7981	684.8547	698.9113	713.3538	727.7964	742.2390
64	671.5846	685.6966	699.8086	713.9206	728.4738	743.0271	757.5804
65	686.5287	700.6968	714.8649	729.0330	743.6964	758.3598	773.0231
66	701.5758	715.8012	730.0266	744.2520	759.0245	773.7971	788.5697
67	716.7283	731.0125	745.2967	759.5809	774.4615	789.3422	804.2228
68	731.9890	746.3339	460.6788	775.0237	790.0109	804.9981	819.9853
69	747.3605	761.7685	776.1765	790.5844	805.6764	820.7684	835.8604
70	762.8457	777.3195	791.7932	806.2670	821.4617	836.6563	851.8510
71	778.4479	792.9907	807.5335	822.0763	837.3711	852.6659	867.9607
72	794.1707	808.7862	823.4017	838.0171	853.4092	868.8012	884.1933
73	810.0174	824.7097	839.4020	854.0943	869.5803	885.0663	900.5523
74	825.9920	840.7657	855.5394	870.3131	885.8893	901.4655	917.0417
75	842.0984	856.9587	871.8190	886.6792	902.3414	918.0036	933.6658
76	858.3410	873.2934	888.2456	903.1983	918.9418	934.6853	950.4289

Table III.4 (Continued)

1	2	3	4	5	6	7	8
77	874.7241	889.7749	904.8256	919.8763	935.6960	951.5157	967.3354
78	891.2525	906.4082	921.5640	936.7197	952.6098	968.5000	984.3902
79	907.9309	923.1989	938.4668	953.7347	969.6891	985.6436	1001.598
80	924.7647	940.1526	955.5405	970.9283	986.9403	1002.952	1018.964
81	941.7587	957.2749	972.7912	988.3074	1004.370	1020.432	1036.494
82	958.9188	974.5723	990.2259	1005.879	1021.984	1038.088	1054.192
83	976.2505	992.0509	1007.351	1023.652	1039.790	1055.927	1072.065
84	993.7598	1009.717	1025.675	1041.632	1057.794	1073.956	1090.119
85	1011.453	1027.578	1043.703	1059.828	1076.005	1092.182	1108.358
86	1029.336	1045.640	1061.945	1078.249	1094.430	1110.610	1126.791
87	1047.415	1063.911	1080.407	1096.903	1113.076	1129.249	1145.422
88	1065.698	1082.398	1099.098	1115.798	1131.951	1148.105	1164.259
89	1084.191	1101.108	1118.026	1134.943	1151.065	1167.187	1183.308
90	1102.901	1120.050	1137.200	1154.349	1170.425	1186.501	1202.577
91	1121.836	1139.232	1156.628	1174.023	1190.039	1206.056	1222.072
92	1141.004	1158.681	1176.319	1193.977	1209.918	1225.859	1241.800

able III.4 (Continued)

1	2	3	4	5	6	7	8
93	1160.411	1178.347	1196.284	1214.220	1230.070	1245.920	1261.770
94	1180.067	1198.299	1216.530	1234.762	1250.504	1266.246	1281.988
95	1199.979	1218.524	1237.069	1255.614	1271.230	1286.847	1302.463
96	1220.155	1239.032	1257.909	1276.786	1292.258	1307.731	1323.203
97	1240.605	1259.834	1279.062	1298.230	1313.599	1329.907	1344.216
98	1261.338	1280.937	1300.537	1320.136	1335.261	1350.386	1365.510
99	1282.361	1302.353	1322.345	1342.537	1357.257	1372.175	1387.094
100	1303.685	1324.091	1344.497	1364.904	1379.595	1394.286	1408.977

atoms and ions. These are listed below:

Atom/ion	$\sigma_{\text{HFS}} \times 10^5$
C (Z=6)	26.57621
Si (Z=14)	88.74195
Co (Z=27)	218.9905
Rb (Z=45)	443.7413
Yb (Z=70)	813.9327
Rb ⁺ (Z=45)	443.1881
Co ⁺⁺ (Z=27)	216.4498

From Table III.4 the extrapolated values for these constants are found to be 28.42582, 88.79022, 220.0591, 444.1385, 806.2670, 443.2170 and 218.2769 respectively. As can be seen here all the extrapolated results excepting that for carbon agree with the directly calculated values within about 1%. Unfortunately we could not check the values for negative ions due to reasons explained earlier in section 2.

For the neutral atoms from $Z = 2$ to $Z = 86$ recently Froese and Malli²⁰ have reported σ_{HF} values calculated using numerical HF wave functions. We shall therefore first compare our extrapolated σ_{HFS} values for the neutral atoms with these available values. For this purposes let us define a percentage parameter Δ as follows:

$$\Delta = \frac{\sigma_{\text{HF}}(\text{cal.}) - \sigma_{\text{HFS}}(\text{ext.})}{\sigma_{\text{HF}}(\text{cal.})} \times 100\% \quad (3.10)$$

We find that from $Z = 10$ to $Z = 86$, $|\Delta|$ remains less than 2.06%, the two values agreeing most favourably in the higher Z (> 44) region where $|\Delta|$ is less than 1%. On the other hand, in the lower

Z region ($Z < 10$), $|\Delta|$ is larger as compared to value of 2.06 for the Z region 10 to 86. $|\Delta|$ value is significantly high for $Z = 4$ and 5.

For comparison of σ_{HF} (extrapolated) values for the neutral atoms reported by Malli and Fraga¹⁸ with the σ_{HF} (calculated)²⁰ values show that in this case a Δ' defined as

$$\Delta' = \frac{\sigma_{\text{HF}}(\text{cal.}) - \sigma_{\text{HF}}(\text{ext.})}{\sigma_{\text{HF}}(\text{cal.})} \times 100\% \quad (3.11)$$

has values less than 1% between $Z = 11$ to $Z = 86$. From $Z = 2$ to $Z = 10$ we find that $|\Delta'|$ has higher values, especially for $Z = 4$ and 5.

It is quite clear that the HF values extrapolated by Malli and Fraga¹⁸ compare better than our HFS values with the HF values directly calculated by Froese and Malli²⁰. However, comparing our directly calculated σ_{HFS} values with the directly calculated σ_{HF} values reported by Froese and Malli²⁰ for the neutral atoms in the higher Z regions (see for example the case of Xe and Rn, where our extrapolated values compare well with our directly calculated values) we find marked differences, namely, our values lie slightly above the σ_{HF} values. Hence, there is little wonder that our extrapolated σ_{HFS} values do not agree so well with the directly calculated σ_{HF} values of Froese and Malli²⁰ in the higher Z regions. On the other hand, we note that for the lower Z region the disagreement between the σ_{HF} (calculated) values on the one hand and σ_{HF} (extrapolated) or σ_{HFS} (extrapolated) values on the other hand is marked.

We shall now compare our σ_{HFS} extrapolated values for singly charged positive and negative ions as well as neutral atoms with corresponding σ_{HF} extrapolated values of Malli and Fraga¹⁸. We shall do

this with help of a parameter Δ'' defined as

$$\Delta'' = \frac{\sigma_{HF}^{(ext.)} - \sigma_{HFS}^{(ext.)}}{\sigma_{HF}^{(ext.)}} \times 100\% \quad (3.12)$$

The behaviour of Δ'' can be summarized as follows:

(i) For Negative Ions

Δ'' is maximum (+18.89%) at $Z = 3$ and decreases rapidly with increasing Z till it becomes +1.43% at $Z = 6$. After this, it becomes negative and remains so till $Z = 39$. In this region $|\Delta''|$ first increases from a value 0.28% at $Z = 7$ to a value 3.03% at $Z = 15$ and then decreases slowly to a value 0.03% at $Z = 39$. From $Z = 39$ to 99 Δ'' again remains positive and in this region it increases slowly from a value 0.15% at $Z = 40$, attains a maximum value 6.18% at $Z = 84$ and then decreases to a value 4.94% at $Z = 99$.

(ii) For Neutral Atoms

Δ'' remains always negative excepting in the region $Z = 70$ to $Z = 78$ in which Δ'' is positive and is less than 0.06%. In this case also it is found that $|\Delta''|$ has larger values in lower Z region, for example between $Z = 3$ to $Z = 7$, $4.62\% < |\Delta''| < 7.26\%$. In the region $Z = 8$ to $Z = 14$ $|\Delta''| > 2.0\%$ and it decreases as Z increases. From $Z = 15$ to $Z = 53$ $|\Delta''| > 1.0\%$ and in this region also $|\Delta''|$ decreases as Z increases. From $Z = 54$ to $Z = 89$, $|\Delta''| < 1.0\%$ and this region includes the region where Δ'' changes sign. From $Z = 90$ to $Z = 100$ $|\Delta''|$ increases from the value 1.11% at $Z = 90$ to a value 3.34% at $Z = 100$.

(iii) For Positive Ions

From $Z = 3$ to $Z = 12$ Δ'' is negative. At $Z = 3$ it has the value -26.36% after which it increases rapidly till it becomes -0.31% at $Z = 12$. From $Z = 13$ to $Z = 24$ Δ'' remains positive and varies from a value 0.03% to a value 0.06% with a maximum of 0.55% at $Z = 17$. From $Z = 25$ to $Z = 101$, $|\Delta''|$ increases slowly from a value 0.05% to a value 8.31% . The marked rise in Δ'' values in the lower Z region ($Z = 3$ to 6) may be noted.

It may be remarked here that the extrapolation of σ values by polynomial fitting has not been reported elsewhere in the literature. Malli and Fraga¹⁸ have used quite a good number of equidistant points with the spacing $\Delta Z = 1$ to obtain the parameters in their extrapolation formula. A procedure like ours may yield better results provided one uses many more number of equidistant points for the polynomial curve fitting of $\sigma_{\text{HFS}}(Z)$, $\sigma_+(Z)$ and $\sigma_-(Z)$. The assumption that in an isoelectronic series the variation of σ_{HFS} with n is linear (see eqn. 3.9) appears to be satisfactory for singly charged negative ions and singly, doubly and triply charged positive ions (see Table III.3). However, if one also takes into account the fact that in an isoelectronic series the variation of σ_{HFS} with n is not strictly linear the extrapolated results will be still better.

III.4 ONE-ELECTRON $\langle r^2 \rangle_{\text{HFS}}$ AND $\langle (1/r) \rangle_{\text{HFS}}$ INTEGRALS

In Tables III.5(a) to III.10(b) we give the one-electron $\langle (1/r) \rangle_{\text{HFS}}$ and $\langle r^2 \rangle_{\text{HFS}}$ integrals for the six isoelectronic series having closed shell configurations.

TABLE III.5(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals For He and He-Like Ions
(in atomic units)

Orbital	Atom or Ion			
	He (Z=2)	Li ⁺ (Z=3)	Be ⁺⁺ (Z=4)	B ⁺⁺⁺ (Z=5)
1s	1.692353	2.688816	3.687247	4.686390

TABLE III.5(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals For He and He-Like Ions
(in atomic units)

Orbital	Atom or Ion			
	He (Z=2)	Li ⁺ (Z=3)	Be ⁺⁺ (Z=4)	B ⁺⁺⁺ (Z=5)
1s	1.233661	.4562010	.2358818	.1438154

TABLE III.6(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Ne and Ne-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	F ⁺ (Z=9)	Ne (Z=10)	Na ⁺ (Z=11)	Mg ⁺⁺ (Z=12)	Al ⁺⁺⁺ (Z=13)
1s	8.686209	9.674532	10.66426	11.65523	12.64740
2s	1.459702	1.674208	1.905055	2.143141	2.385024
2p	1.224343	1.501521	1.766667	2.026862	2.284320

TABLE III.6(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Ne and Ne-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	F ⁻ (Z=9)	Ne (Z=10)	Na ⁺ (Z=11)	Mg ⁺⁺ (Z=12)	Al ⁺⁺⁺ (Z=13)
1s	.0411972	.0331366	.0272169	.0227443	.0192840
2s	1.253038	.9379720	.7149596	.5602813	.4501943
2p	2.261021	1.167901	.7716762	.5578509	.4251932

TABLE III.7(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Ar and Ar-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	Cl ⁻ (Z=17)	Ar (Z=18)	K ⁺ (Z=19)	Ca ⁺⁺ (Z=20)	Sc ⁺⁺⁺ (Z=21)
1s	16.61769	17.61168	18.60626	19.60123	20.59664
2s	3.335000	3.574997	3.816020	4.058006	4.300859
2p	3.263073	3.508145	3.733712	3.999774	4.246315
3s	.9085731	1.014082	1.124725	1.237171	1.350244
3p	.7287677	.8670131	.9968465	1.122329	1.245018

TABLE III.7(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Ar and Ar-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	Cl ⁻ (Z=17)	Ar (Z=18)	K ⁺ (Z=19)	Ca ⁺⁺ (Z=20)	Sc ⁺⁺⁺ (Z=21)
1s	.0111167	.0098877	.0088511	.0079688	.0072117
2s	.2296437	.1999384	.1755656	.1553302	.1383553
2p	.1974789	.1694872	.1469993	.1286661	.1135280
3s	2.740615	2.190934	1.778645	1.472167	1.239742
3p	4.848103	3.063240	2.241863	1.744289	1.408489

TABLE III.8(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Kr and Kr-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	Br ⁻ (Z=35)	Kr (Z=36)	Rb ⁺ (Z=37)	Sr ⁺⁺ (Z=38)	Yt ⁺⁺⁺ (Z=39)
1s	34.56284	35.56074	36.55865	37.55651	38.55464
2s	7.690897	7.933545	8.176437	8.419593	8.662996
2p	7.681940	7.926779	8.171777	8.416955	8.662342
3s	2.555054	2.655965	2.757874	2.860735	2.964360
3p	2.451171	2.555202	2.660120	2.765857	2.872244
3d	2.213689	2.331645	2.448906	2.565646	2.681867
4s	.7924641	.8595955	.9295000	.9998496	1.069911
4p	.6172106	.7136266	.8008618	.8830415	.9618581

TABLE III.8(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Kr and Kr-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	Br ⁻ (Z=35)	Kr (Z=36)	Rb ⁺ (Z=37)	Sr ⁺⁺ (Z=38)	Yt ⁺⁺⁺ (Z=39)
1s	.0025431	.0024017	.0022717	.0021520	.0020415
2s	.0436816	.0410650	.0386743	.0364841	.0344728
2p	.0335953	.0315109	.0296129	.0278795	.0262922
3s	.3553883	.3291984	.3056253	.2843486	.2651165
3p	.3665159	.3367654	.3103177	.2867244	.2656290
3d	.4006720	.3548165	.3167692	.2847855	.2576249
4s	3.260243	2.760123	2.358994	2.043426	1.791953
4p	6.047894	4.110990	3.182819	2.598540	2.188924

TABLE III.9(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Xe and Xe-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	I ⁻ (Z=53)	Xe (Z=54)	Cs ⁺ (Z=55)	Ba ⁺⁺ (Z=56)	La ⁺⁺⁺ (Z=57)
1s	52.53380	53.53245	54.53112	55.52980	56.52852
2s	12.08436	12.32968	12.57497	12.82035	13.06592
2p	12.10709	12.35362	12.60022	12.84698	13.09369
3s	4.425780	4.531497	4.637411	4.743518	4.849828
3p	4.357952	4.464928	4.572061	4.679354	4.786814
3d	4.233984	4.343754	4.453545	4.563369	4.673244
4s	1.816629	1.875521	1.934812	1.994505	2.054509
4p	1.718907	1.780066	1.841549	1.903352	1.965407
4d	1.487501	1.558119	1.628314	1.698118	1.767506
5s	.6471380	.6955125	.7452553	.7947942	.8437100
5p	.5133094	.5834614	.6459941	.7042430	.7595786

TABLE III.9(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Xe and Xe-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	I ⁻ (Z=53)	Xe (Z=54)	Cs ⁺ (Z=55)	Ba ⁺⁺ (Z=56)	La ⁺⁺⁺ (Z=57)
1s	.0010966	.0010559	.0010175	.0009811	.0009466
2s	.0177697	.0170723	.0164152	.0157950	.0152090
2p	.0133039	.0127702	.0122678	.0117942	.0113476
3s	.1209684	.1155134	.1104124	.1056356	.1011558
3p	.1152148	.1097735	.1047026	.0999693	.0955439
3d	.0961722	.0911181	.0864518	.0821338	.0781297
4s	.6530695	.6141442	.5784314	.5455954	.5153800
4p	.7142121	.6668985	.6239877	.5849632	.5494163
4d	.9231758	.8373293	.7635982	.6997714	.6441481
5s	4.621491	3.985993	3.472002	3.062033	2.730306
5p	7.995519	5.754346	4.613719	3.870546	3.335510

TABLE III.10(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Rn and Rn-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	At ⁻ (Z=85)	Rn (Z=86)	Fr ⁺ (Z=87)	Ra ⁺⁺ (Z=88)	Ac ⁺⁺⁺ (Z=89)
1s	84.50423	85.50267	86.50208	87.50115	88.50028
2s	19.99218	20.23963	20.48709	20.73459	20.98212
2p	20.04333	20.29148	20.53962	20.78786	21.03601
3s	7.819240	7.925555	8.031947	8.138420	8.244972
3p	7.784354	7.891396	7.998502	8.105675	8.212918
3d	7.731000	7.839436	7.947901	8.056406	8.164950
4s	3.485092	3.542082	3.599304	3.656742	3.714400
4p	3.406437	3.464294	3.522369	3.580652	3.639143
4d	3.245243	3.305472	3.365859	3.426396	3.487087
4f	2.972118	3.039827	3.107237	3.174384	3.241305
5s	1.543259	1.582739	1.622446	1.662373	1.702488
5p	1.446536	1.488095	1.529813	1.571681	1.613653
5d	1.216142	1.265952	1.315327	1.364278	1.412793
6s	.5901732	.6292007	.6689931	.7082840	.7468013
6p	.4685455	.5269177	.5780863	.6251246	.6693497

TABLE III.10(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Rn and Rn-Like Ions
(in atomic units)

Orbital	Atom or Ion				
	At ⁻ (Z=85)	Rn (Z=86)	Fr ⁺ (Z=87)	Ra ⁺⁺ (Z=88)	Ac ⁺⁺⁺ (Z=89)
1s	.0004225	.0004126	.0004031	.0003940	.0003851
2s	.0065152	.0063573	.0062051	.0060583	.0059166
2p	.0047878	.0046702	.0045569	.0044476	.0043423
3s	.0397014	.0386608	.0376600	.0366969	.0357697
3p	.0363185	.0353430	.0344057	.0335047	.0326380
3d	.0276578	.0268794	.0261329	.0254168	.0247294
4s	.1836266	.1779381	.1724939	.1672811	.1622870
4p	.1857978	.1797542	.1739843	.1684728	.1632045
4d	.1887003	.1817829	.1752259	.1690054	.1630986
4f	.1910365	.1814848	.1726915	.1645711	.1570490
5s	.8443985	.8049436	.7680794	.7335895	.7013025
5p	.9491576	.8989544	.8525864	.8096853	.7699565
5d	1.324399	1.220740	1.130113	1.050414	.979913
6s	5.316570	4.657310	4.117835	3.682630	3.326413
6p	9.109462	6.738046	5.508361	4.697481	4.107246

The contributions to χ and σ from an electron in an atom are respectively proportional to average of the square and the average of the reciprocal of its distance from the nucleus. Hence, the electron nearest to the nucleus will contribute largest to σ and least to χ . This fact is confirmed from the tables of the one-electron integrals given here.

Let $\sigma'_{\text{HFS}}(Z, n, l)$ represent the contribution to $\sigma_{\text{HFS}}(Z) \times 10^5$ of an atom or ion with nuclear charge Z from an electron with principal quantum number n and angular momentum quantum number l . To explain the behaviour of $\sigma'_{\text{HFS}}(Z, n, l)$ we shall now discuss the quantity $d\sigma'_{\text{HFS}}(Z, n, l)$ defined as

$$d\sigma'_{\text{HFS}}(Z, n, l) = \sigma'_{\text{HFS}}(Z, n, l) - \sigma'_{\text{HFS}}(Z, n, l+1) \quad (3.13)$$

It is seen from the Tables III.5(a), III.6(a), III.7(a), III.8(a), III.9(a) and III.10(a) that $d\sigma'_{\text{HFS}}(Z, n, l)$ shows the following trends:

(i) For Fixed n and l Values

$d\sigma'_{\text{HFS}}(Z, n, l)$ decreases as Z increases. For example, as one goes from $Z = 9$ (F^-) to $Z = 39$ (Yt^{+++}) $d\sigma'_{\text{HFS}}(Z, 2, 0)$ decreases regularly from +0.4177495 to +0.0011598. At $Z = 53$ (I^-) and $Z = 89$ (Ac^{+++}) the $d\sigma'_{\text{HFS}}(Z, 2, 0)$ values are -0.0403455 and -0.0956571 respectively. Thus, for each set of (n, l) values there seems to be a possibility of getting a Z value where $d\sigma'_{\text{HFS}}(Z, n, l)$ is negligibly small.

(ii) For Fixed Z and l Values

$d\sigma'_{\text{HFS}}(Z, n, l)$ increases as n increases. For example, in Table III.10(a) as one goes from $n = 2$ to $n = 6$, $d\sigma'_{\text{HFS}}(86, n, 0)$ increases

regularly from -0.0920275 to +0.1815470; in Table III.9(a) as one goes from $n = 3$ to $n = 4$ $d\sigma'_{\text{HFS}}(53, n, 1)$ increases from +0.2200364 to +0.4107335.

(iii) For Fixed Z and n Values

$d\sigma'_{\text{HFS}}(Z, n, 1)$ increases as l increases. For example, in Table III.10(a) as one goes from $l = 0$ to $l = 2$ $d\sigma'_{\text{HFS}}(84, 4, 1)$ increases regularly from +0.1380700 to +0.4715066.

Malli and Fraga¹⁸ have shown on the basis of their calculations on Xe that $\sigma'_{\text{HF}}(Z, n, 1)$ is apparently independent of l for all n values. Thus they concluded that the mean distance of an electron from the nucleus in an atom depends almost exclusively upon the principal quantum number of the shell into which the electron is accommodated. The general behaviour of the per-electron contributions to the nuclear magnetic shielding value is, however, as explained above. It is accidental that the overall behaviour of $d\sigma'_{\text{HFS}}(Z, n, 1)$ is such that at $Z = 54$ (Xe) its value is very small for all n and l values which led Malli and Fraga¹⁸ to conclude that $\sigma'(54, n, 1)$ is almost independent of l for all n values. Further, since it is true that the behaviour of $\langle (1/r) \rangle$ and $\langle r \rangle$ are somewhat related, both $f_1(r) = 1/r$ and $f_2(r) = r$ being odd functions of r , one can comment on the mean distance between an electron and the nucleus from a study of the behaviour of $\langle (1/r) \rangle$. Thus, from our study we may conclude that the mean distance of an electron from the nucleus is not always independent of its angular momentum quantum number.

From Tables III.5(b), III.6(b), III.7(b), III.8(b), III.9(b) and III.10(b) one concludes that the behaviour of per-electron

contribution to the HFS diamagnetic susceptibility of an atom is qualitatively opposite to that of $\sigma'(Z, n, 1)$.

III.5 AN ALTERNATIVE METHOD FOR EXTRAPOLATING σ_{HFS} VALUES IN AN ISOELECTRONIC SERIES

An alternative method for obtaining σ values will be now discussed. This is based on the concept of the stability of the SCF wave functions under one-electron perturbations. We shall, therefore first briefly outline the concept of stability of a wave function under a perturbation following Hall².

For the quantum mechanical evaluation of physical properties of atoms and ions one usually makes use of approximate wave functions. Often, one finds that the evaluated value disagrees with the experimental value, even though the wave function used is capable of reproducing a good energy value. A change in the wave function which does not alter the energy value to an appreciable extent is sometimes found to alter the evaluated physical property to an appreciable extent. According to Hall² this erratic behaviour is due to the use of an unstable wave function in the evaluation of the physical property in question. Hall has therefore introduced the concept of stability of a wave function under a perturbation. The Schrodinger equation for the perturbed system can be written as

$$(\mathcal{H} + \lambda P)\psi = E\psi \quad (3.14)$$

where \mathcal{H} = non-relativistic Hamiltonian and λ is a parameter depending on the strength of the perturbation P , which may be a relativistic term, some additional internal operator, a term of interaction of the system with an external field or in the simplest case a change in one of the

terms already present in the unperturbed Hamiltonian. If we assume that $\Psi(\lambda)$ is normalized and the operators \mathcal{H} and P are such that $E(\lambda)$ is differentiable with respect to λ at least for $\lambda = 0$, we get

$$E(\lambda) = \int_0^{\infty} \Psi^* \mathcal{H} \Psi d\tau$$

so that

$$\begin{aligned} \frac{dE(\lambda)}{d\lambda} &= \int_0^{\infty} \frac{d\Psi^*}{d\lambda} \mathcal{H} \Psi d\tau + \int_0^{\infty} \Psi^* \mathcal{H} \frac{d\Psi}{d\lambda} d\tau + \int_0^{\infty} \Psi^* P \Psi d\tau \end{aligned} \quad (3.15)$$

If one imposes the condition

$$\int_0^{\infty} \frac{d\Psi^*}{d\lambda} \mathcal{H} \Psi d\tau + \int_0^{\infty} \Psi^* \mathcal{H} \frac{d\Psi}{d\lambda} d\tau = 0 \quad (3.16)$$

on the wave functions we get

$$\int_0^{\infty} \Psi^* P \Psi d\tau = \frac{dE(\lambda)}{d\lambda} \quad (3.17)$$

The wave functions obeying the condition (3.16) (the condition of stability under the perturbation P) are known as stable wave functions under the perturbation P . They may be stable for all λ values or for some specific λ values. Hall has shown that SCF wave functions are

stable under one-electron perturbations. Further, treating a change in the atomic number Z appearing in the potential energy term of the unperturbed Hamiltonian as a one-electron perturbation and applying the condition of stability for wave functions he has deduced the relationship

$$\langle L \rangle = Z \frac{\partial E(Z)}{\partial Z} \quad (3.18)$$

for the total potential energy $\langle L \rangle$ due to the electrons and the nucleus with atomic number Z . $E(Z)$, of course, represents the total energy of the atom or ion with atomic number Z . By analogy with the well-known expression for the nuclear diamagnetic shielding in atoms derived by Lamb¹⁶ Hall has obtained the relation

$$\sigma_n(Z) = - \frac{\alpha^2}{3} \frac{\partial E_n(Z)}{\partial Z} \quad (3.19)$$

(α being the fine structure constant and n the number of the electrons) Hall himself has used the above equation to evaluate the nuclear magnetic shielding constants for the two-electron isoelectronic series H^- , He , Li^+ , Be^{++} . He used the series expansion for $E(Z)$ given earlier by Hylleraas and Midtdal²⁴ for two-electron systems which has the form,

$$E_n(Z) = (a_n)Z^2 + (b_n)Z + (c_n) + \frac{(d_n)}{Z} + \frac{(e_n)}{Z^2} + \frac{(f_n)}{Z^3} + \frac{(g_n)}{Z^4} + \dots \quad (3.20)$$

It may be pointed out that Hall and Rees²⁵ have also used a similar procedure for evaluating the shielding values for isoelectronic series having 2 to 6 electrons. These workers also used a polynomial similar to that used by Hall², which is due to ^{the} well-known treatment of Hylleraas²⁶. Using the relationship (3.19) Ellison^{14,15} has calculated the σ values for atoms and ions with the number of electrons n equal

to 2 upto 10 and nuclei of charge Z equal to $n-1$ to 10. He found slopes $\frac{\partial E_n(Z)}{\partial Z}$ using a simple ascending power series Z -expansion.

It is thus a straightforward matter to evaluate the shielding values for the various isoelectronic series provided one has a relationship governing the dependence of the total SCF energy values on Z in each of the isoelectronic series such as the one given by equation (3.20), for example.

III.5(A) A REVIEW OF Z-EXPANSION OF ENERGIES IN MULTIELECTRON ATOMS AND IONS

For two-electron atoms and ions it was shown originally by Hylleraas²⁶ that the variation of the total energy with Z can be obtained by perturbation approach where the term $(1/r_{12})$ is chosen as the perturbation term in the Hamiltonian. This leads to an equation of the form (3.20). The coefficients in the expansion have been obtained for the He isoelectronic series by Hylleraas and Midtdal²⁴. The leading term in the expansion is a Z^2 term and the successive terms are Z^1 , Z^0 , Z^{-1} , ...etc. That this form of the expansion for non-relativistic total energy $E_n(Z)$ is valid for n -electron systems has been shown by Lowdin²⁷. Total $E_n^{HF}(Z)$ can also be expressed by a similar expansion in decreasing powers starting with Z^2 . The perturbation approach was employed by Lowdin to demonstrate this. A considerable amount of work has been done regarding such Z -expansion for He isoelectronic series^{24,26,28-36}. In recent years the form of Z -expansion in the unrestricted Hartree-Fock formalism for He-like and Li-like systems has also been investigated³⁷⁻⁴⁰. Such expansions are of interest in the study of correlation energies⁴¹. Wave functions can also be expanded⁴²⁻⁴⁶ in Z and thus the calculations of energies as well as

other expectation values become a simpler task. Dalgarno and coworkers^{28,47,48} have outlined details of calculation of atomic properties using this procedure in atomic systems with upto ten electrons. As mentioned before the coefficients in the Z expansion can be obtained by perturbation approach. The coefficient of Z^2 term of the energy expansion is simply the energy of the system using hydrogenic wave functions while the successive terms correspond to first, second, etc. order terms of the perturbation. A rigorous perturbation approach can therefore yield these coefficients, as has been shown by Hylleraas²⁶, Hylleraas and Midtdal²⁴ and Midtdal⁴⁹ for two-electron systems. The work of Linderberg and Shull⁵⁰ and Linderberg^{51,52} may also be cited in this regard. The Z -expansion of non-relativistic energy in many-electron systems from this view point has been studied especially by Layzer^{46,53,54}. The relativistic Z -dependent theory of many electron system has also been discussed⁵⁵.

Ionisation potentials and electron affinities of atoms can also be expressed in a series form similar to the series for $E_n(Z)$. Empirically it was shown by Glockler⁵⁶ that ionisation potentials can be expressed in the form $I_n(Z) = \alpha Z^2 + \beta Z + \gamma$. Edlen⁵⁷ has used a similar series expansion starting with Z^2 to extrapolate electron affinities. Scherr et al.⁵⁸ have used experimental ionisation potential data to fit a four-term polynomial in Z and have obtained semi-empirical values of non-relativistic total energies in three-to ten-electron isoelectronic series. This polynomial has the form

$$E_n(Z) = Z^2 \sum_{i=0}^{\infty} \epsilon_{in} Z^{-i} \quad (3.21)$$

which has been theoretically justified. Crossley and Coulson⁵⁹ have shown that these empirical formulae can be justified on the basis of the $E_n(Z)$ expansion described earlier. The well-known formula of Moseley for the X-ray lines is also a case in point. For negative atomic ions it has been pointed out by Johnson and Rohrlich⁶⁰ and Edie and Rohrlich⁶¹ that even a four-term formula of the type

$$I_n(Z) = \alpha Z^2 + \beta Z + \gamma + \delta Z^{-1} \quad (3.22)$$

is not satisfactory. These authors have therefore fitted the ionisation potential data to an empirical series disregarding the fact that the form of equation (3.22) rests on sound theoretical basis. Clementi⁶² and Ellison and Huff⁶³ have used empirical power series expansion in ascending powers of Z for the total energy

$$E_n(Z) = \bar{A}_n + \bar{B}_n Z + \bar{C}_n Z^2 + \bar{D}_n Z^3 + \dots \quad (3.23)$$

Although the HF energy data can be fitted to such a series the meaning of the various coefficients in such an expansion is not clear. On the other hand in the series expansion of the type (3.20) the coefficients have theoretical significance. It is easily seen that if one uses only three terms in the expansion then both equations (3.20) and (3.23) become identical. The term involving Z^{-1} in equation (3.20) has been found to be usually smaller than the relativistic correction⁵⁴. The rate at which a given expansion converges is known to depend strongly on the value of $Z-n$, the degree of ionization⁵⁴.

On the basis of the present review it may be expected that an expansion in Z using three or four terms in the form (3.20) should be

fairly adequate to represent energy values in an isoelectronic series.

III.5(B) Z-EXPANSION OF HF ENERGIES AND NUCLEAR MAGNETIC SHIELDING

Total E_n^{HF} values for various isoelectronic series containing two to twentyseven electrons have been recently made available by Clementi³. In the Appendix we have demonstrated that these total HF energies can be satisfactorily fitted by means of a three-term polynomial of the form (3.20). Using the relationship (3.19) G_{HF} values could be calculated. In the Appendix we report results of these calculations and compare them with those calculated directly using HF wave functions by Malli and Fraga¹⁸. A similar treatment for G_{HFS} , though possible in principle, is not given here since total E_n^{HFS} values are not readily available. The problem of calculating total E_{HFS} from the orbital energies and the various integrals has been recently underlined by Lindgren⁶⁴.

III.6 CONCLUSION

It may be noted that just as in the case of the rare gas atoms, the HFS wave functions give a good description of the self-consistent fields of closed-shell ions as well both for large and small distances from the nucleus. An empirical extrapolation procedure has been outlined to obtain the shielding values for atoms and ions. The values obtained by this procedure appear to be quite satisfactory and it is pointed out that the reliability of the extrapolated values can be improved by calculations on some more systems as well so as to provide better polynomial fitting. A theoretical justification for the $S_+(Z)$ values can be given in terms of

a three-term energy polynomial. It can be readily seen that since

$$\begin{aligned}\sigma &= -\frac{\alpha^2}{3} \frac{\partial E_n(Z)}{\partial Z} = -\frac{\alpha^2}{3} \left[\frac{\partial}{\partial Z} \{A_n Z^2 + B_n Z + C_n\} \right] \\ &= -\frac{\alpha^2}{3} (2A_n Z + B_n)\end{aligned}$$

for each member of the isoelectronic series, as Z increases by one unit we see that σ changes by a constant term $-(2/3)\alpha^2 A_n$. The fact that $\sigma_-(Z)$ is different from $\sigma_+(Z)$ can be perhaps attributed to the fact that negative ions are not easily fitted by means of the three-term formula^{60,61,63}.

From the study of the various $\langle (1/r) \rangle_{\text{HFS}}$ integrals we have concluded that the mean distance of an electron from the nucleus in an atom is not always roughly independent of its angular momentum quantum number. The alternative method discussed here for the evaluation of nuclear magnetic shielding values in an isoelectronic series, using the total energy values, is found to be a powerful method.

REFERENCES

1. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Inc., Englewood Cliffs, New Jersey (1963).
2. G.G. Hall, Phil. Mag., 6, 249 (1961).
3. E. Clementi, IBM J. Res. Develop., 9, 2 (1965) and the extended supplement to this paper, entitled 'Tables of Atomic Functions'.
4. C. Barter, R.G. Meisenheimer and D.P. Stevenson, J. Phys. Chem., 64, 1312 (1960).
5. G. Malli and S. Fraga, Theoret. chim. Acta (Berlin), 5, 284 (1966).
6. F. Herman (private communication) has also confirmed this behaviour of HFS wave functions.
7. T.W. Sidwell and R.P. Hurst, J. Chem. Phys., 37, 203 (1962).
8. K.E. Banyard, J. Chem. Phys., 33, 832 (1960).
9. A. Gold and R.S. Knox, Phys. Rev., 113, 834 (1959).
10. C.C.J. Roothaan and A. Weiss, Rev. Mod. Physics, 32, 194 (1960).
11. T.G. Strand and R.A. Bonham, J. Chem. Phys., 40, 1686 (1964).
12. R.A. Bonham and T.G. Strand, J. Chem. Phys., 40, 3447 (1964).
13. W.C. Dickenson, Phys. Rev., 80, 563 (1950).
14. F.O. Ellison, J. Chem. Phys., 40, 2421 (1964).
15. F.O. Ellison, J. Chem. Phys., 41, 2018 (1964).
16. E. Hylleraas and S. Skavlem, Phys. Rev., 79, 117 (1950).
17. W.E. Lamb, Phys. Rev., 60, 817 (1941).
18. G. Malli and S. Fraga, Theoret. chim. Acta (Berlin), 5, 275 (1966).
19. M.L. Rustgi and P. Tewari, J. Chem. Phys., 39, 2590 (1963).
20. C. Froese and G. Malli, Slater Symposium, University of Florida, 1967 Jan. (G. Malli, private communication).
21. B.Y. Tong and L.J. Sham, Phys. Rev., 144, 1 (1966).
22. I.S. Sokolinkoff and R.M. Redheffer, "Mathematics of Physics and Modern Engineering, McGraw Hill Book Company, Inc., New York (1958), Chap. IX, Sec. 6—Sec. 11.

23. W.R. Graves, Polynomial Curve Fitting, IBM 1620 Users Group Library, White Plains, New York (1961).
24. E.A. Hylleraas and J. Midtdal, Phys. Rev., 103, 829 (1956); See also Phys. Rev., 109, 1013 (1958).
25. G.G. Hall and D. Rees, Proc. Phys. Soc. (London), 79, 444 (1962).
26. E.A. Hylleraas, Z. Physik, 65, 209 (1930).
27. P.O. Lowdin, J. Mol. Spectr., 3, 46 (1959).
28. A. Dalgarno, Proc. Phys. Soc. (London), 75, 439 (1960).
29. M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London), 77, 165 (1961).
30. R.E. Knight and C.W. Scherr, Phys. Rev., 128, 2675 (1962).
31. R.E. Knight and C.W. Scherr, J. Chem. Phys., 37, 2503 (1962).
32. C.S. Sharma and C.A. Coulson, Proc. Phys. Soc. (London), 80, 81 (1962).
33. R.E. Knight and C.W. Scherr, Rev. Mod. Phys., 35, 431 (1963).
34. C.W. Scherr and R.E. Knight, Rev. Mod. Phys., 35, 436 (1963).
35. C.W. Scherr and R.E. Nkight, J. Chem. Phys., 40, 3034 (1964).
36. A. Froman and G.G. Hall, J. Mol. Spectr., 7, 410 (1961).
37. C.S. Sharma, Proc. Phys. Soc. (London), 80, 839 (1962).
38. A.L. Stewart, Proc. Phys. Soc. (London), 83, 1033 (1964).
39. C.A. Coulson, Proc. Phys. Soc. (London), 84, 511 (1964).
40. C.A. Coulson and A. Hibbert, Proc. Phys. Soc. (London), 91, 33 (1967).
41. Z. Horak in "Modern Quantum Chemistry", Istanbul Lectures, Ed. O. Sinanoglu, Part II, Academic Press, New York (1965), page 7 and the references therein.
42. D.R. Hartree, "The Calculation of Atomic Structures", John Wiley & Sons, Inc., New York (1957), page 118.
43. C. Froese, Proc. Roy. Soc. (London), A239, 311 (1957); A244, 390 (1958).
44. C. Froese, Phys. Rev., 116, 900 (1959).
45. C. Froese, Can. J. Phys., 41, 50 (1963).

46. D. Layzer, Phys. Rev., 132, 735 (1963).
47. M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London), A261, 565 (1961).
48. M. Cohen, A. Dalgarno and J.M. McNamee, Proc. Roy. Soc. (London), A269, 550 (1962).
49. J. Midtdal, Phys. Rev., 138, A1010 (1965).
50. J. Linderberg and H. Shull, J. Mol. Spectr., 5, 1 (1960).
51. J. Linderberg, Phys. Rev., 121, 816 (1961).
52. J. Linderberg, J. Mol. Spectr., 9, 95 (1962).
53. D. Layzer, Ann. Phys. (New York), 8, 271 (1959).
54. D. Layzer, Z. Horak, M.N. Lewis and D.P. Thompson, Ann. Phys. (New York), 29, 101 (1964).
55. D. Layzer and J. Bahcall, Ann. Phys. (New York), 17, 177 (1962).
56. G. Glockler, Phys. Rev., 36, 111 (1934).
57. B. Edlen, J. Chem. Phys., 33, 98 (1960).
58. C.W. Scherr, J.N. Silverman and F.A. Matsen, Phys. Rev., 127, 830 (1962).
59. R.J.S. Crossley and C.A. Coulson, Proc. Phys. Soc. (London), 81, 211 (1963).
60. H.R. Johnson and F. Rohrllich, J. Chem. Phys., 30, 1608 (1959).
61. J.W. Edie and F. Rohrllich, J. Chem. Phys., 36, 623 (1962).
62. E. Clementi, J. Chem. Phys., 38, 996, 1001. (1963).
63. F.O. Ellison and N.T. Huff, J. Chem. Phys., 39, 2051 (1963).
64. I. Lindgren, Arkiv Fysik, 31, 59 (1966).
65. L.C. Allen, J. Chem. Phys., 34, 1156 (1961).

CHAPTER IV

FERMI-CONTACT INTERACTION TERM AND HARTREE-FOCK-SLATER WAVE FUNCTIONS

CHAPTER IV

FERMI CONTACT INTERACTION AND HARTREE-FOCK-SLATER WAVE FUNCTIONS

IV.1 INTRODUCTION

As part of a test of the Hartree-Fock-Slater wave functions of Herman and Skillman¹ we have investigated as to how far these wave functions are capable of reproducing a reasonably good value of the atomic hyperfine splitting constant corresponding to the "Fermi-Contact Interaction"² term. This term, due to the interaction between the spin magnetic moment of an electron and the spin magnetic moment of a nucleus, appears in the hyperfine structure splitting of the atomic energy levels as well as in the spin-spin interaction observed in electron-spin-resonance and in nuclear magnetic resonance^{3,4}. A brief theoretical discussion of this interaction will be given in section 2. As we shall see there the closed-shell core gives no contribution to this term. The only contribution appearing will be

due to the unpaired valence electron and that too is nonvanishing only for an electron occupying a s-orbital. The present investigation will therefore provide a check on the reliability of the HFS single determinantal wave functions for open-shell configurations and especially for the s-orbitals with an unpaired electron. The evaluation of these hyperfine splitting constants provides a test of the wave function very near the nucleus. We have calculated the hyperfine structure constants for the ground states of $\text{Li}(1s^2 2s^1)$, $\text{Na}(1s^2 2s^2 2p^6 3s^1)$, $\text{K}(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1)$, $\text{Cu}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1)$ and $\text{Ca}^+(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1)$ using the Hartree Fock-Slater wave functions for the s-orbital corresponding to the unpaired electron in each of them. The details of the calculations are given in section 3. In section 4 the results of these calculations are reported. Here we also compare our results with other available calculations and experimental data. It is found that the results of the present calculation compare favourably with experimental data.

IV.2 THEORETICAL CONSIDERATIONS

The point charge model of the nucleus having a large mass and a charge Ze was found to be inadequate to explain all the details of atomic spectra. The very small splittings of spectral lines, known as hyperfine structure, can be explained only on the basis of the fact that nuclei have electric and magnetic multipoles in general, so that, we can have electric interaction between the nucleus and the surrounding electron charges as well as magnetic interaction between the magnetic nucleus and the electron spin and orbital magnetic moments. Nuclei do not possess electric dipole moment as can be shown from parity considerations⁵.

Nuclei with spin angular momentum (in units of \hbar) $I \geq \frac{1}{2}$ have electric quadrupole moments while those with $I \geq 2$ have electric moments of order 4 and so on. On the other hand, nuclei can have magnetic dipole moments when $I \geq \frac{1}{2}$ and so on. If the nuclear spin is zero no magnetic or electric multipole moments can exist.

We shall be dealing here only with the magnetic dipole moment and its interaction with electrons. The nuclear spin magnetic moment μ_I , the electron spin magnetic moment μ_S and the electron orbital magnetic moment μ_L can be expressed by the relations:

$$\begin{aligned}\mu_I &= \gamma \hbar I \\ \mu_S &= 2 \beta S \\ \mu_L &= 2 \beta L\end{aligned}\tag{4.1}$$

where I , S and L are nuclear spin, electron spin and electron orbital angular momentum operators in units of \hbar . γ is the nuclear magnetogyric ratio and β is the Bohr magneton. In its general form the magnetic interaction between the nuclear spin magnetic moment and the electron spin and orbital magnetic moments is given by

$$\begin{aligned}\mathcal{H}_{eN} = 2\beta \hbar \gamma I \cdot & \left[\left\{ (r)^{-3} \vec{I} \right\} + \left\{ 3(r)^{-5} (\vec{r}) (\vec{S} \cdot \vec{r}) - (r)^{-3} \vec{S} \right\} \right. \\ & \left. + \left\{ \frac{8\pi}{3} \delta(\vec{r}) \vec{S} \right\} \right]\end{aligned}\tag{4.2}$$

The first term on right hand side represents the interaction of a point dipole γI with the orbital motion of the electron while the second term represents the usual dipole-dipole interaction between two point

dipoles $\gamma \hbar I$ and $2\beta S$. The last term is the term which is of interest to us here and it represents an interaction of the electron at the site of the nucleus. This term is called the Fermi-Contact term because it appears due to the fact that the probability of finding an electron at the site of the nucleus is finite and was first derived by Fermi² on the basis of Dirac's relativistic theory of electron. Several other workers (for example see refs. 6 and 7) have also derived the Hamiltonian \mathcal{H}_{eN} on the basis of this approach. It appears to be a general belief that the interaction Hamiltonian \mathcal{H}_{eN} can be derived only on the basis of Dirac's relativistic theory of electrons. However, it has been shown by Nierenberg⁸ that this Hamiltonian can also be derived solely from classical electron magnetic theory. Ferrell⁹ has also derived the contact interaction term on the basis of purely classical static magnetism principles. For a lucid derivation of this Hamiltonian on the basis of Dirac's relativistic theory of electrons we may refer to a paper by Blinder¹⁰. It must also be pointed out here that this problem of deriving \mathcal{H}_{eN} has been treated^{11,12} on the basis of quantum field theory as well.

It can easily be seen that the magnetic interaction energy corresponding to the contact interaction term in \mathcal{H}_{eN} can be written as

$$E_{eN(c)} = \frac{16\pi}{3} \beta \hbar \gamma |\Psi(0)|^2 (\vec{I} \cdot \vec{S}) \quad (4.3)$$

where $\Psi(0)$ is the value of the wave function Ψ at the origin. It is obvious that this energy will be nonvanishing only for those electrons which have finite probability at the origin ($r = 0$). Since the radial part of the wave function $R(r)$ corresponding to an electron having angular

momentum quantum number l has the form $R(r) = \sum_{k=0} a_k(r)^{l+k}$ near the origin, one concludes that s-electrons (having $l=0$) only have nonvanishing $\Psi(0)$ value. Thus $E_{eN(C)}$ will be nonzero only for s-electrons.

For an atomic system having many electrons the extension of equation (4.3) will be as follows

$$E_{eN(C)}(S) = \frac{16\pi}{3} \beta k \gamma \sum_i \pm |\Psi_i(0)|^2 (\vec{I} \cdot \vec{S}_i) \quad (4.4)$$

where the S within parenthesis in the left hand side of the equation shows that this energy is due to the s-electrons and summation is over all s-electrons of the system. The sign is taken plus for electrons of positive spin and minus for electrons of negative spin. For a completely filled s-orbital having one up and one down spin in it the net contribution to the above energy goes to zero unless one takes into account the fact that $\Psi_{ns\uparrow}$ is slightly different from $\Psi_{ns\downarrow}$ through the phenomenon of core polarization^{13,14}. The presence of an unpaired electron has an effect on the wave function of the other electrons. Actually the exchange forces acting on the electrons with spins parallel to the unpaired^e spin are different from the forces acting on electrons with opposite spin. This causes a slight difference between $\Psi_{ns\uparrow}$ and $\Psi_{ns\downarrow}$. This is taken into account in the Unrestricted Hartree Fock (UHF) formalism. It will be therefore seen that even if the unpaired electron is in an orbital other than s it can interact with the nucleus in this manner due the core polarization phenomenon. However, we shall be dealing here only with the interaction between the unpaired electron in an s-orbital and the nucleus and also neglect core polarization effects. As far as the

present Hartree-Fock-Slater wave functions are concerned they are restricted in the sense that $\psi_{ns\uparrow}$ is same as $\psi_{ns\downarrow}$. With these assumptions we can write

$$E_{eN(C)}(S) = \frac{16\pi}{3} \beta \hbar \gamma |\psi_{s-val}(0)|^2 (\vec{I} \cdot \vec{S}) \quad (4.5)$$

taking the valence electron to have an "up" spin. For an s-electron having spin $+\frac{1}{2}$, we have $j = l+s = \frac{1}{2}$ so that

$$(\vec{I} \cdot \vec{S}) = \frac{1}{2} \left\{ k(k+1) - I(I+1) - \frac{3}{4} \right\} \quad (4.6)$$

where $\vec{k} = \vec{j} + \vec{I}$. k can therefore have the values $(I+\frac{1}{2})$ and $(I-\frac{1}{2})$.

Thus the energy difference between the corresponding hyperfine levels is given by

$$\begin{aligned} \Delta E_{eN(C)}(S) &= \frac{16\pi}{3} \hbar \beta \gamma |\psi_{s-val}(0)|^2 \\ &\quad \cdot \frac{1}{2} \left\{ (I+\frac{1}{2})(I+\frac{1}{2}+1) - (I-\frac{1}{2})(I-\frac{1}{2}+1) \right\} \\ &= \frac{8\pi}{3} \beta \hbar \gamma |\psi_{s-val}(0)|^2 (2I+1) \end{aligned} \quad (4.7)$$

The hyperfine splitting constant $a_C(S)$ is given by

$$\begin{aligned} a_C(S) &= \frac{2\Delta E}{(2I+1)} = \frac{16\pi}{3} \hbar \beta \gamma |\psi_{s-val}(0)|^2 \\ &= \frac{16\pi}{3} \beta \left(\frac{\mu_N}{I} \right) |\psi_{s-val}(0)|^2 \\ &= \frac{16\pi}{3} \beta \mu_N \left(\frac{\mu_N}{I} \right) |\psi_{s-val}(0)|^2 \end{aligned} \quad (4.8)$$

where μ_N is the nuclear magneton and μ' is the nuclear spin magnetic moment in units of μ_N .

IV.3 CALCULATIONS OF a_C

As pointed out earlier we have calculated $a_C(S)$ for the systems Li, Na, K, Cu and Ca^+ . It is clear from equation (4.8) that a calculation of $a_C(S)$ would require for each system the value of nuclear spin I in units of \hbar , the value of μ' , the nuclear magnetic moment in units of nuclear magnetons and $|\Psi(0)|^2$ for the corresponding unpaired s-electron. The values of I and μ' have been taken from Ramsey's Book⁵. In order to get the values of $|\Psi_{s-val}(0)|^2$ we first note that in general the $\Psi(r, \theta, \phi)$'s are of the form

$$\Psi_{nlm}(r, \theta, \phi) = \frac{(-1)^{(m+|m_l|)/2}}{\sqrt{4\pi}} \sqrt{\frac{(2l+1)(l-|m_l|)!}{(l+|m_l|)!}} R_{nl}(r) P_l^{|m_l|}(\cos \theta) \exp(im\phi) \quad (4.9)$$

so that for a s-orbital having $l = 0$ and $m = 0$ the wave function is of the form

$$\Psi_{ns}(r, \theta, \phi) = \frac{R_{ns}(r)}{\sqrt{4\pi}} \quad (4.10)$$

which is independent of the angles θ and ϕ . Hence

$$|\Psi(0)|^2 = \frac{R_{ns}(0)^2}{4\pi} \quad (4.11)$$

Thus, the problem is reduced to one of finding out the value of the radial function at the origin. We make use of the Hartree-Fock-Slater radial wave functions¹ given as x vs. $P_{nl}(x)$ tables where x is related to r by the relation $r = \mu x$, μ being the Thomas-Fermi parameter ($\mu = 0.88534138xZ^{-\frac{1}{2}}$). Also, as is well-known, $P_{nl}(x)$ and $R_{nl}(x)$ are related as $xR_{nl}(x) = P_{nl}(x)$ and $P_{nl}(x)$ is normalized as $\int P_{nl}^2(r)dr = 1 = \int P_{nl}^2(x)\mu dx$. In order to get the value of $R_{ns}(0)$ for the ns valence orbital in each case we assume that near the origin the radial wave function for the s -orbitals behaves as

$$R_{ns}(r) = \frac{P_{ns}(r)}{r} = (a_{ns}) + (b_{ns})r + (c_{ns})r^2 + (d_{ns})r^3 \quad (4.12)$$

and expect it to be valid for four consecutive points $r_1 = \mu x_1$, $r_2 = \mu x_2$, $r_3 = \mu x_3$ and $r_4 = \mu x_4$ near the origin. This gives us the following set of simultaneous equations

$$\left. \begin{aligned} \frac{P_{ns}(r_1)}{r_1} &= (a_{ns}) + (b_{ns})r_1 + (c_{ns})r_1^2 + (d_{ns})r_1^3 \\ \frac{P_{ns}(r_2)}{r_2} &= (a_{ns}) + (b_{ns})r_2 + (c_{ns})r_2^2 + (d_{ns})r_2^3 \\ \frac{P_{ns}(r_3)}{r_3} &= (a_{ns}) + (b_{ns})r_3 + (c_{ns})r_3^2 + (d_{ns})r_3^3 \\ \frac{P_{ns}(r_4)}{r_4} &= (a_{ns}) + (b_{ns})r_4 + (c_{ns})r_4^2 + (d_{ns})r_4^3 \end{aligned} \right\} \quad (4.13)$$

Sets of such equations are then solved by Crouts method^{15,16}

of elimination to get the values of the unknown constants a_{ns} , b_{ns} , c_{ns} and d_{ns} . This has been done on an IBM 1620 Computer at I.I.T., Kanpur. From equation (4.12) it is obvious that

$$\left| R_{ns}(r) \right|_{r=0} = a_{ns} = \left| R_{ns}(0) \right| \quad (4.14)$$

and therefore from equation (4.11) we get

$$\left| \psi_{ns}(0) \right|^2 = \frac{(a_{ns})^2}{4\pi} \quad (4.15)$$

Use of equation (4.8) then yields the $a_0(S)$ values.

IV.4 RESULTS AND DISCUSSION

Table IV.1 collects the values of $\left| \psi(0) \right|_{HFS}^2$ for the ns-valence orbital in each of the system studied in the present investigation. For comparison this table also includes the relevant results of Goodings¹⁷. The $\left| \psi(0) \right|_{UHF}^2$ are the values in which the contributions from the closed (ns) orbitals of the core have been included due to the nonzero values of

$$\rho_{ns} = \left| \psi_{ns+}(0) \right|^2 - \left| \psi_{ns-}(0) \right|^2 \quad (4.16)$$

for each completely filled s-orbital of the core.

From a comparison of the entries in column (3) and (4) it is obvious that the effect of the core polarization is significant. However, if we compare the entries of column (2) and (3) we see that the HFS wave functions give higher values of $\left| \psi_{s-val}(0) \right|^2$ than those given by HF wave functions. Furthermore, the difference $\left| \psi_{s-val}(0) \right|_{HFS}^2 - \left| \psi_{s-val}(0) \right|_{HF}^2$

TABLE IV.1

Values of $|\Psi(0)|_{\text{HFS}}^2$ for the Valence (ns) Orbitals for Some
Systems in Ground State
(in atomic units)

Atom/Ion	Present Calculation $ \Psi_{\text{val}}(0) _{\text{HFS}}^2$	Calculated by Goodings ^(a)	
		$ \Psi(0) _{\text{HF}}^2$	$ \Psi(0) _{\text{UHF}}^2$ $= \sum_{\text{ns}} (\rho_{\text{ns}})_{\text{UHF}} + \Psi_{\text{val}}(0) _{\text{UHF}}^2$
Li	0.21521	0.1637	0.2247
Na	0.76076	0.5667	0.8469
K	1.04102	0.6879	0.8542
Cu	4.63727	-	-
Ca ⁺	2.56216	-	-

a) See ref. 17; The wave functions used in this work were of the HF and UHF types (ref. 18).

increases as we go to higher Z values. For lower Z values our

$|\Psi_{\text{s-val}}(0)|_{\text{HFS}}^2$ values are closer to $|\Psi(0)|_{\text{UHF}}^2$ (column 4 of Table IV.1).

This is surprising because we completely neglect core polarization.

Table IV.2 lists the values of $a_{\text{C}}(\text{S})_{\text{HFS}}$ constants evaluated here. This Table also contains the results of other calculations and experimental data wherever available. It can be seen from this table that surprisingly, the HFS wave functions are able to reproduce the experimental values of the hyperfine structure constants fairly well. In comparison to the HF values

TABLE IV.2

HFS Hyperfine Structure Constants $a_C(S)_{\text{HFS}}$ for the Ground State of Some Systems
(in Mc/Sec)

Other Calculations

System	Present Calculation $a_C(S)_{\text{HFS}}$	Experimental Value (a)	Hartree-Fock (HF)			Unrestricted Hartree-Fock (UHF)					Configuration Interaction (j)	Using Empirical Potential
			(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)		
1	2	3	4	5	6	7	8	9	10	11	12	13
Li^6	141.567		110									
Li^7	373.869	401.786	291	284	289.55(1)	285(1)	390	390.55	354.795	372-396	396.7465	$246^k 387^m$
Na^{22}	354.490		246									
Na^{23}	899.985	885.805	625	669	636.34(2)	792(2)	764			837		$623^k 810^l$
Na^{24}	256.903		178									
K^{38}	388.753		259									
K^{39}	217.402	230.862	145	143			178					
K^{40}	270.343		180									

able IV.2 (Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
K ⁴¹	119.499		80									
K ⁴²	473.585		380									
Ca ⁺⁴³	771.605		580									
Cu ⁶³	4964.147		3561									
Cu ⁶⁴	1484.316		959									
Cu ⁶⁵	5899.489		3813									

- a) Values determined by Kusch and Taub (ref. 20).
b) Calculated by Malli and Fraga (ref. 21) using Malli's analytic HF functions and analytic HF functions of ref. 22.
c) Calculated by Goodings (ref. 17) using his own numerical HF wave functions (ref. 18).
d) 1. Calculated by Sachs (ref. 23) using HF wave function of ref. 24.
2. Calculated by Sachs (ref. 25) using his own HF wave functions.
e) 1. Calculated by Cohen, Goodings and Heine (ref. 26) using HF wave function of Fock and Petrashen (ref. 27).
2. Calculated by Cohen, Goodings and Heine (ref. 26) using HF wave function of Fock and Petrashen (ref. 28).
f) Calculated by Goodings (ref. 17) using his own numerical UHF wave functions (ref. 18).
g) Calculated by Sachs using his own UHF wave function (ref. 23).
h) Calculated by Sachs using his own Projected UHF wave function (ref. 23).
i) Calculated by Cohen, Goodings and Heine using their own Perturbation UHF wave functions (ref. 26).
j) Calculated by Nesbet using configuration interaction approach (ref. 29).
k) See reference 30.
l) See reference 32.
m) See reference 31.

our present results on $a_0(S)$ using HFS formalism are seen to be uniformly higher. It was pointed out in Chapters II and III that the Slater approximation overemphasizes the role of exchange. This overemphasis leads to greater contraction of the wave function as can be seen from the calculated $|\psi_{s-\text{val}}(0)|_{\text{HFS}}^2$ values. It may be noted that inclusion of core polarization improves considerably the conventional HF values, although even then the agreement between these and the experimental values is not very good. In our present HFS calculations we have not taken into account the core polarization effects. In view of these facts one is led to the conclusion that the agreement between the HFS values and experiment is somewhat fortuitous. The restriction $\psi_{ns\uparrow} = \psi_{ns\downarrow}$ can be removed in the HFS formalism also¹³ and ^{such} calculations have been carried out for Fe by Wood and Pratt¹⁹. The core polarization in this case was shown to be large. These workers also concluded that the Slater form of the exchange potential overemphasizes the effect of exchange. Concerning the present HFS calculations it may be remarked here that as one goes to higher Z values (i) the relativistic corrections become important (note that the HFS wave functions used here are non-relativistic), (ii) correlation effects become important especially for the valence orbital which contributes the most to $\sum_i |\psi_i(0)|^2$ in the unrestricted formalism and (iii) the number of the closed (ns) orbitals increases which makes the assumption

$$\sum_{\text{closed orbitals}} \rho_{ns} = 0$$

less and less justified. The results obtained here using HFS functions appear, however, to be promising.

IV.5 CONCLUSION

Values of atomic hyperfine splitting constants calculated using the HFS wave functions agree well with experimental data. This agreement, it is pointed out, may be a result of the overemphasis of the exchange potential in the Slater formalism. The results can be probably improved by modifications of the exchange potential (for example use of reduced Slater potential, correction of the averaged potential in the inner regions etc. , inclusion of core polarization and relativistic effects).

REFERENCES

1. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Inc., Englewood Cliffs, New Jersey (1963).
2. E. Fermi, Z. Physik, 60, 320 (1930); E. Fermi and E. Segre, Z. Physik, 82, 729 (1933).
3. A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford (1961).
4. C.P. Slichter, "Principles of Magnetic Resonance", Harper and Row, New York (1963).
5. N.F. Ramsey, "Molecular Beams", Oxford University Press, Oxford (1956).
6. H.B.G. Casimir, "On the Interaction between Atomic Nuclei and Electrons", Vol. 11, page 36, Teylers Tweede Genootshaafs, Haarlem (1936).
7. R.A. Frosch and H.M. Foley, Phys. Rev., 88, 1337 (1952).
8. W.A. Nierenberg, Ann. Rev. Nuclear Science, Vol.7, Palo Alto, Calif., Annual Reviews, Inc., 1957, Page 353.
9. R.A. Ferrell, Amer. J. Phys., 28, 484 (1960).
10. S.M. Elinder, J. Mol. Spectr., 5, 17 (1960).
11. R. Arnowitt, Phys. Rev., 92, 1002 (1953).
12. R. Karplus and A. Klein, Phys. Rev., 85, 972 (1952); 87, 848 (1952).
13. G.W. Pratt, Jr., Phys. Rev., 102, 1303 (1956).
14. V. Heine, Phys. Rev., 107, 1002 (1957).
15. P.D. Croust, Trans. AIEE, 60, 1235 (1941).
16. R. Wooldridge, "An Introduction to Computing", Oxford University Press, London (1962) page 90.
17. D.A. Goodings, Phys. Rev., 123, 1706 (1961).
18. D.A. Goodings, Ph.D. Thesis, Cambridge University (1960).
19. J.H. Wood and G.W. Pratt, Jr., Phys. Rev., 107, 995 (1957).
20. P. Kusch and H. Taub, Phys. Rev., 75, 1477 (1949).
21. G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin), 6, 278 (1966).

22. E. Clementi, "Tables of Atomic Functions", an extended supplement to the paper in IBM J. Res. Develop. (9, 2 (1965)).
23. L.M. Sachs, Phys. Rev., 117, 1504 (1960).
24. C.C.J. Roothaan, L.M. Sachs and A. Weiss, Rev. Mod. Phys., 32, 186 (1960).
25. L.M. Sachs, "A Theoretical Study of Simple Many-Electron Systems", Report No. ANL-6310, Argonne National Laboratory, May 1961.
26. M.H. Cohen, D.A. Goodings and V. Heine, Proc. Phys. Soc. (London), 73, 811 (1959).
27. V. Fock and M.J. Petrashen, Phys. Z. Sowjet, 8, 547 (1935).
28. V. Fock and M.J. Petrashen, Phys. Z. Sowjet, 6, 368 (1934).
29. R.K. Nesbet, Phys. Rev., 118, 681 (1960).
30. H. Jones and B. Schiff, Proc. Phys. Soc. (London), A67, 217 (1954).
31. W. Kohn, Phys. Rev., 96, 590 (1954).
32. T. Kjeldaas and W. Kohn, Phys. Rev., 101, 66 (1956).

CHAPTER V

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND
DIAMAGNETIC SUSCEPTIBILITY AND NUCLEAR
MAGNETIC SHIELDING VALUES FOR NEUTRAL
ATOMS HAVING OPEN-SHELL CONFIGURATIONS

CHAPTER V

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND DIAMAGNETIC SUSCEPTIBILITY AND NUCLEAR MAGNETIC SHIELDING VALUES FOR NEUTRAL ATOMS HAVING OPEN-SHELL CONFIGURATION

V.1 INTRODUCTION

In Chapters II and III we have seen that the single determinantal Hartree-Fock-Slater (HFS) wave functions of Herman and Skillman¹ are capable of reproducing diamagnetic susceptibility (χ) values and nuclear magnetic shielding (σ) values for closed-shell atoms and ions to sufficiently good degree of accuracy. In Chapter IV we discussed the use of these HFS wave functions in calculation of hyperfine structure constants of the Fermi-Contact term in open-shell configurations having unpaired s-electron in their valence orbitals. These results showed that the use of the single determinantal form of the HFS wave functions for open-shell configurations results in fairly good values for these constants. The present chapter

concerns itself with the calculation of diamagnetic susceptibility (χ_{HFS}) and nuclear magnetic shielding (σ_{HFS}) values for open-shell configurations. In these systems the paramagnetic contribution to the susceptibility is of course by far the most important one. The calculations of the diamagnetic susceptibility have been made with a view to compare them with the corresponding HF values. Atoms from three different regions of the Periodic Table were chosen: i) Region of lower Z values ($Z = 3$ to $Z = 15$), ii) Region of medium Z values ($Z = 45$ to $Z = 53$) and iii) Region of higher Z values ($Z = 81$ to $Z = 90$). Our results are presented and compared with HF calculations wherever available in section 3.

V.2 THEORETICAL DETAILS AND METHOD OF CALCULATION

The details of the quantum mechanical calculation of χ and σ values is the same as that adopted in Chapters II and III. The various one-electron integrals required were evaluated in the same manner as described in Chapters II and III. As in the case of calculations of χ and σ values for closed-shell atoms and ions (see Chapter III) we have used in the present calculations also the 441-point mesh HFS wave functions. These were obtained by using a Herman-Skillman type computer program on an IBM 7044 Computer at I.I.T., Kanpur. The details of the evaluation of the 441-point mesh HFS wave functions are the same as those described in Chapter III, section 2.

V.3 RESULTS AND DISCUSSION

The diamagnetic susceptibility values (χ_{HFS}) and nuclear magnetic shielding constants (σ_{HFS}) for the various neutral atoms having

open-shell configurations are given in Tables V.1 and V.2 respectively. The calculations of diamagnetic susceptibility values and nuclear magnetic shielding constants using Hartree-Fock wave functions for atoms have been carried out in recent years²⁻¹¹. Our Tables V.1 and V.2 also compare the results of the present investigation with these recent calculations using HF wave functions. The agreement is found to be satisfactory in general.

Since the exchange interaction is attractive, its inclusion draws in the radial wave functions closer to the nucleus. If the free-electron exchange approximation overemphasizes the exchange term we would expect the HFS wave functions to produce the $|\chi_{\text{HFS}}|$ and σ_{HFS} values respectively lower and higher than the corresponding $|\chi_{\text{HF}}|$ and σ_{HF} values. From Table V.1 we observe that χ_{HFS} values are lower than χ_{HF} values whereas from Table V.2 we observe that σ_{HFS} values are higher than σ_{HF} values. This confirms the fact that Slater's free-electron exchange approximation overemphasizes the exchange term. It was noted earlier in Chapter III that σ_{HFS} (extrapolated) values do not agree well with σ_{HF} (calculated) or σ_{HF} (extrapolated) values. We are now in a position to clearly say that these differences arise out of the fact that the HFS formalism leads to an increase in the σ values consistently in comparison with the HF formalism. The presently calculated σ_{HFS} values can be compared with our earlier extrapolated values (see Chapter III). The agreement between these is seen to be good. In view of the fact that the single determinantal form of the HFS wave functions has been used in the present calculations the results may be judged as encouraging.

In Tables V.3(a), V.3(b) and V.3(c) we list the one-electron

$\langle r^2 \rangle_{\text{HFS}}$ integrals while in Tables V.4(a), V.4(b) and V.4(c) we list the one-electron $\langle (1/r) \rangle_{\text{HFS}}$ integrals in atomic units.

V.4 CONCLUSION

The present calculations of χ_{HFS} and σ_{HFS} values and their comparison with the HF calculations show that the single determinantal form of the HFS wave functions can be successfully employed for the calculation of the diamagnetic susceptibility and nuclear magnetic shielding values even for open-shell configurations. Of course, one should bear in mind the limitations of such an approach. One should also remember the fact that the functions used here are non-relativistic and have been obtained using the averaged exchange potential. In view of these limitations the present results are encouraging.

TABLE V.1

HFS Diamagnetic Susceptibility Values (χ_{HFS}) for Neutral Atoms with
Open-Shell Configuration
(All Values in -1×10^6 cgs emu/mole)

Z Region	Atom and its At. No. Z	χ_{HFS} Present Calculation	Other HF Calculations		
			(a)	(b)	(c)
1	2	3	4	5	6
	Li(Z=3)	13.93525	14.764	15.2	14.76
	Be(Z=4)	13.47607	13.729	14.1	13.72
	B(Z=5)	12.54516	12.556	12.7	
	C(Z=6)	10.92854	10.930	11.0	
	N(Z=7)	9.612183	9.565	9.6	
i) Lower	O(Z=8)	8.580326	8.846	8.9	
	F(Z=9)	7.757992	8.110	8.1	8.119
	Na(Z=11)	19.92166	21.500	18.1	
	Mg(Z=12)	22.01124	23.451	22.2	
	Al(Z=13)	25.44953	26.518	24.6	
	Si(Z=14)	24.49036	25.559	24.9	
	P(Z=15)	23.02190	23.985	23.2	
	Rh(Z=45)	38.68676			
	Ag(Z=47)	36.52428			
	In(Z=49)	45.23064			

Table V.1 (Continued)

1	2	3	4	5	6
ii)Medium	Sn(Z=50)	46.69590			
	Sb(Z=51)	46.95879	.		
	Te(Z=52)	46.79985			
	I(Z=53)	46.43282			
	Tl(Z=81)	56.46090			
	Pb(Z=82)	58.59770			
	Bi(Z=83)	59.42255			
	Po(Z=84)	59.74448			
iii)Higher	At(Z=85)	59.79493			
	Fr(Z=87)	85.92642			
	Ac(Z=89)	92.39008			
	Th(Z=90)	90.50310			

- a) Values reported by Malli and Fraga (ref. 10) using analytic HF wave functions of reference 15.
- b) Evaluated by Strand and Bonham (ref. 5) using an approximate analytic expression for the HF potential of neutral atoms by fitting the radial electron density of analytic HF functions.
- c) Calculated by Sidwell and Hurst (ref. 3) using single determinantal analytic SCF functions of Roothaan type (Li and Be - ref. 12, F - ref. 13).

TABLE V.2

HFS Nuclear Magnetic Shielding Values ($\sigma_{\text{HFS}} \times 10^5$) for Neutral Atoms with Open-Shell Configuration

Z Region	Atom and its	σ_{HFS}		Other HF Calculations							
	At. No.	Z	Calculation	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
1	2	3	4	5	6	7	8	9	10	11	
	Li(Z=3)	10.46193	10.145	10.145	10.138	10.145	10.141	10.421	10.145	10.145	
	Be(Z=4)	15.26742	14.976	14.926	14.914	14.926	14.920	15.303	14.932	14.926	
	B(Z=5)	20.61980	20.199			20.199		20.203	20.207		
	C(Z=6)	26.57621	26.074			26.074		26.068	26.102		
	N(Z=7)	33.12500	32.547			32.547		32.524	32.561		
	O(Z=8)	40.26027	39.511			39.511		39.443	39.526		
	F(Z=9)	47.97854	47.071	47.831		47.071		47.003	47.083		
	Na(Z=11)	64.07842	62.887			62.890			63.087		
	Mg(Z=12)	72.08729	70.859			70.560			71.222		
	Al(Z=13)	80.27002	78.986			78.988			79.392		

i) Lower

Table V.2 (Continued)

1	2	3	4	5	6	7	8	9	10	11
	Si(Z=14)	88.74195	87.406			87.409			87.870	
	P(Z=15)	97.49545	96.111			96.114			96.664	
	Rh(Z=45)	443.7413				440.014				
	Ag(Z=47)	471.2904				467.385				
	In(Z=49)	498.5122				494.872				
ii)Medium	Sn(Z=50)	512.2206				508.555				
	Sb(Z=51)	526.0315				522.343				
	Te(Z=52)	539.9407				536.200				
	I(Z=53)	553.9492				550.164				
	Tl(Z=81)	994.7222				989.416				
	Pb(Z=82)	1011.292				1006.092				
	Bi(Z=83)	1027.933				1022.713				
iii)Higher	Po(Z=84)	1044.638				1039.386				

Table V.2 (Continued)

1	2	3	4	5	6	7	8	9	10	11
iii) Higher At (Z=85)		1061.414				1055.993				
Fr (Z=87)		1094.828								
Ac (Z=89)		1128.292								
Th (Z=90)		1145.207								

- a) Values reported by Malli and Fraga (ref. 9) using analytic HF wave functions of reference 15.
- b) Values calculated by Sidwell and Hurst (ref. 3) using single determinantal analytic HF-SCF functions of Roothaan type (Li and Be - ref. 12, F-ref. 13).
- c) Calculated by Ormand and Matsen using radially correlated wave functions (ref. 2).
- d) Values reported by Froese and Malli (ref. 11) using numerical HF wave functions.
- e) Calculated by Ormand and Matsen using radially uncorrelated wave functions (ref. 2).
- f) Calculated by Ellison (ref. 7 and 8); calculated using rescaled functions obtained by Ellison and Huff (ref. 14).
- g) Evaluated by Bonham and Strand (ref. 6) using their approximate analytic expression of HF potential of atoms upto Z=36 (ref. 5).
- h) Calculated by Rustgi and Tewari (ref. 4) using single determinantal analytic SCF functions of Roothaan, Sachs and Weiss (ref. 12).

TABLE V.3(a)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms (Z=3 to 15)
 with Open-Shell Configuration
 (in atomic units)

Atom	Orbitals				
	1s	2s	2p	3s	3p
Li(Z=3)	0.4249377	16.74517			
Be(Z=4)	0.2260155	8.281618			
B(Z=5)	0.1404947	4.424543	6.709799		
C(Z=6)	0.0957177	2.840655	3.962971		
N(Z=7)	0.0693633	2.004756	2.662792		
O(Z=8)	0.0525548	1.499958	1.932184		
F(Z=9)	0.0411840	1.168534	1.475205		
Na(Z=11)	0.2722270	0.7088893	0.7545129	19.15435	
Mg(Z=12)	0.0227508	0.5587071	0.5551088	11.64922	
Al(Z=13)	0.0192920	0.4514131	0.4279910	7.060035	14.50387
Si(Z=14)	0.0165631	0.3724412	0.3412575	5.063199	8.985137
P(Z=15)	0.0143729	0.3126493	0.2790845	3.906315	6.308999

TABLE V.3(b)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms ($Z=45$ to 53)
with Open-Shell Configuration
(in atomic units)

Orbital	Atom						
	Rh (Z=45)	Ag (Z=47)	In (Z=49)	Sn (Z=50)	Sb (Z=51)	Te (Z=52)	I (Z=53)
1s	.0015273	.0013985	.0012853	.0012338	.0011854	.0011397	.0010966
2s	.0252676	.0230037	.0210295	.0201358	.0192974	.0185101	.0177697
2p	.0190881	.0173330	.0158085	.0151202	.0149758	.0138713	.0133038
3s	.1824618	.1633580	.1470772	.1398213	.1330813	.1268108	.1209672
3p	.1778232	.1581286	.1415163	.1341643	.1273642	.1210630	.1152132
3d	.1579234	.1377743	.1212984	.1141578	.1076342	.1016487	.0961704
4s	1.122983	.9817410	.8508616	.7940002	.7423985	.6955497	.6529544
4p	1.319291	1.138208	.9642074	.8905097	.8249022	.7663652	.7139707
4d	2.632592	2.118470	1.487131	1.293530	1.142908	1.021577	.9214645
5s	14.44534	13.33346	7.847865	6.515451	5.621596	4.950612	4.419637
5p			16.55976	11.85132	9.316835	7.716354	6.594255

TABLE V.3(c)

One Electron $\langle r^2 \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms (Z=81 to 90) with Open-Shell Configuration
(in atomic units)

Orbital	Atom								
	Tl(Z=81)	Pb(Z=82)	Bi(Z=83)	Po(Z=84)	At(Z=85)	Fr(Z=87)	Ac(Z=89)	Th(Z=90)	
1s	.0004656	.0004542	.0004433	.0004327	.0004225	.0004031	.0003851	.0003765	
2s	.0072091	.0070257	.0068490	.0066790	.0065152	.0062051	.0059166	.0057798	
2p	.0053054	.0051685	.0050367	.0049099	.0047878	.0045569	.0043423	.0042406	
3s	.0443068	.0430840	.0419107	.0407840	.0397074	.0376600	.0357699	.0348771	
3p	.0406473	.0394962	.0383928	.0373343	.0363184	.0344057	.0326382	.0318044	
3d	.0311326	.0302054	.0293188	.0284703	.0276578	.0261329	.0247297	.0240697	
4s	.2091228	.2023064	.1957949	.1895728	.1836252	.1724954	.1622950	.1575165	
4p	.2130678	.2057484	.1987758	.1921309	.1857960	.1739861	.1632140	.1581857	
4d	.2205581	.2118980	.2037269	.1960032	.1886976	.1752286	.1631129	.1575142	
4f	.2392854	.2254127	.2128589	.2014472	.1910300	.1726981	.1570791	.1501205	
5s	1.034883	.9816767	.9323415	.8866290	.8442603	.7681937	.7017422	.6718153	
5p	1.201547	1.129090	1.063279	1.003418	.9488487	.8527823	.7706424	.7342775	
5d	1.966296	1.750678	1.579670	1.439326	1.321469	1.130885	.9822576	.9289143	
1	2	3	4	5	6	7	8	9	

Table W.3(c) (Continued)

1	2	3	4	5	6	7	8	9
6s	8.422599	7.151579	6.285307	5.625348	5.095625	4.118105	3.414787	3.166651
6p	17.55879	12.92713	10.38774	8.762793	7.610259	5.475718	4.302188	3.934797
6d							9.606651	8.114773
7s						43.29666	26.43382	23.83085

TABLE V.4(a)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms (Z=3 to 15)
 with Open-Shell Configuration
 (in atomic units)

Atom	Orbitals				
	1s	2s	2p	3s	3p
Li(Z=3)	2.764665	0.3648878			
Be(Z=4)	3.753451	0.5473552			
B(Z=5)	4.379683	0.7595448	0.6186704		
C(Z=6)	5.725849	0.9527002	0.8079257		
N(Z=7)	6.712382	1.1378100	0.9873776		
O(Z=8)	7.699366	1.3187869	1.1615492		
F(Z=9)	8.686771	1.4972988	1.3325623		
Na(Z=11)	10.66359	1.9068146	1.7729322	0.3231721	
Mg(Z=12)	11.65413	2.1422632	2.0265114	0.4309405	
Al(Z=13)	12.64565	2.3799649	2.2774549	0.5555742	0.3967641
Si(Z=14)	13.63788	2.6184790	2.5261240	0.6575841	0.5061510
P(Z=15)	14.63070	2.8573579	2.7731086	0.7514107	0.6036765

TABLE V.4(b)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms (Z=45 to 53)
with Open-Shell Configuration
(in atomic units)

Orbital	Atom						
	Rh(Z=45)	Ag(Z=47)	In(Z=49)	Sn(Z=50)	Sb(Z=51)	Te(Z=52)	I(Z=53)
1s	44.54509	46.54242	48.53921	49.53782	50.53650	51.53499	52.53380
2s	10.12649	10.61537	11.10460	11.34938	11.59428	11.83927	12.08438
2p	10.13711	10.62935	11.12172	11.36799	11.61429	11.86067	12.10711
3s	3.586640	3.795292	4.004684	4.109689	4.214888	4.320263	4.425803
3p	3.507010	3.718949	3.931392	4.037834	4.144423	4.251140	4.357979
3d	3.354076	3.574576	3.794621	3.904537	4.014405	4.124225	4.234010
4s	1.371656	1.471928	1.584298	1.641799	1.699805	1.758158	1.816751
4p	1.257976	1.358181	1.476209	1.536583	1.597291	1.658168	1.719108
4d	.9276842	1.030529	1.193106	1.270074	1.344562	1.417164	1.488255
5s	.3678306	.3835399	.4953605	.5416547	.5829104	.6218079	.6592123
5p			.3506775	.4111038	.4606632	.5045327	.5450863

TABLE V.4(c)

One Electron $\langle 1/r \rangle_{\text{HFS}}$ Integrals for Ground State Neutral Atoms (Z=81 to 90) with Open-Shell Configuration
(in atomic units)

Orbital	Atom								
	Tl(Z=81)	Pb(Z=82)	Bi(Z=83)	Po(Z=84)	At(Z=85)	Fr(Z=87)	Ac(Z=89)	Th(Z=90)	
1	2	3	4	5	6	7	8	9	
1s	80.50685	81.50612	82.50549	83.50421	84.50418	86.50204	88.50027	89.49941	
2s	19.00273	19.24999	19.49744	19.74477	19.99218	20.48708	20.98211	21.22966	
2p	19.05096	19.29901	19.54709	19.79522	20.04334	20.53962	21.03601	21.28425	
3s	7.394683	7.500732	7.606823	7.713000	7.819246	8.031946	8.244944	8.351538	
3p	7.356765	7.463577	7.570449	7.677378	7.784363	7.998504	8.212890	8.320165	
3d	7.297508	7.405854	7.514214	7.622599	7.731010	7.947901	8.164917	8.273454	
4s	3.259495	7.315515	3.371802	3.428339	3.485104	3.599286	3.714304	3.772061	
4p	3.177269	3.234198	3.291385	3.348809	3.406452	3.522351	3.639038	3.697607	
4d	3.005950	3.065507	3.125259	3.185184	3.245260	3.365835	3.486955	3.547644	
4f	2.697076	2.766580	2.835563	2.904069	2.972145	3.107200	3.241108	3.307620	

Table V.4(c) (Continued)

1	2	3	4	5	6	7	8	9
5s	1.386941	1.425720	1.464785	1.504025	1.543358	1.622333	1.701934	1.741725
5p	1.280484	1.321994	1.363599	1.405192	1.446699	1.529655	1.612953	1.654412
5d	1.006309	1.061893	1.115204	1.166774	1.216939	1.314968	1.411419	1.458435
6s	.4689228	.5067371	.5399338	.5710232	.6006497	.6683724	.7375089	.7677623
6p	.3344165	.3858549	.4272212	.4632463	.4961281	.5787019	.6549475	.6864561
6d							.4488037	.4859899
7s						.1995420	.2608095	.2751951

REFERENCES

1. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Inc., Englewood Cliffs, New Jersey (1963).
2. F.T. Ormand and F.A. Matsen, J. Chem. Phys., 30, 368 (1959).
3. T.W. Sidwell and R.P. Hurst, J. Chem. Phys., 37, 203 (1962).
4. M.L. Rustgi and P. Tewari, J. Chem. Phys., 39, 2590 (1963).
5. T.G. Strand and R.A. Bonham, J. Chem. Phys., 40, 1686 (1964).
6. R.A. Bonham and T.G. Strand, J. Chem. Phys., 40, 3447 (1964).
7. F.O. Ellison, J. Chem. Phys., 40, 2421 (1964).
8. F.O. Ellison, J. Chem. Phys., 41, 2018 (1964).
9. G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin), 5, 275 (1966).
10. G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin), 5, 284 (1966).
11. C. Froese and G. Malli, Slater Symposium, University of Florida, 1967, January (G. Malli, Private Communication).
12. C.C.J. Roothaan, L.M. Sachs and A. Weiss, Rev. Mod. Phys., 32, 186 (1960).
13. L.C. Allen, J. Chem. Phys., 34, 1156 (1961).
14. F.O. Ellison and N.T. Huff, J. Chem. Phys., 39, 2051 (1963).
15. E. Clementi, IBM J. Res. Develop., 9, 2 (1965) and the extended supplement to this paper entitled "Tables of Atomic Functions".

CHAPTER VI

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND
QUADRUPOLE ANTISHIELDING FACTORS OF
ATOMS AND IONS

CHAPTER VI

HARTREE-FOCK-SLATER WAVE FUNCTIONS AND QUADRUPOLE ANTISHIELDING FACTORS OF ATOMS AND IONS

VI.1 INTRODUCTION

In the presence of a perturbing electrostatic field, distortions are produced in the electronic charge distribution of atoms and ions. These distortions may be expressed in terms of a series of induced multipole (dipole, quadrupole, octupole,.... etc.) moments and are referred to as multipole polarizations. Due to these distortions there are changes in the electric field and its gradients (of various orders) at the site of the nucleus and these changes are expressed in terms of multipole (dipole, quadrupole,.... etc.) shielding or antishielding factors, the words shielding and antishielding denoting the signs.

Dipole polarizability is related to dielectric constant hence it has been investigated since long. But the quadrupolar and higher order

polarizabilities got the attention of workers only since last fifteen years or so.

In general, the problem has been theoretically looked upon as a perturbation problem. The source of perturbation may have various types of positions with regard to the nucleus and the electronic charge distribution. The nucleus itself may have an electric quadrupole moment, for example. This may perturb the surrounding spherical electron charge distribution of the core and thus modify the field gradients. However, to make the idea of multipole polarizabilities and the associated shielding factors clear, we shall take a simpler situation where the perturbation is caused by an electric charge 1 a.u. placed at a distance R away from the atomic nucleus on the z -axis. The total electrostatic interaction between this charge and the atom or ion will be (in atomic units)

$$V = \frac{Z}{R} - \sum_{i=1}^N \frac{1}{r_i} \quad (6.1)$$

where Z represents the nuclear charge and r_i represents the distance of the i -th electron of the N -electron atom or ion from the perturbing charge. Let us now further assume that the perturbing charge is located completely outside the atom or ion so that it is possible to expand the above interaction using Legendre Polynomials in terms of the distances r_i ($i = 1, 2, \dots, N$) of the electron from the nucleus. Thus we get

$$V = \left[\frac{(Z-N)}{R} \right] + \left[- \sum_{L=1}^{\infty} \sum_{i=1}^N \frac{(r_i)^L}{(R)^{L+1}} P_L(\cos \theta_i) \right] \quad (6.2)$$

where $P_L(\cos \theta_i)$ ($L = 1, 2, \dots$) represent the Legendre Polynomials of

various orders. The first term on the right hand side of equation (6.2) is constant and hence will not polarize the electron core. The second term, however, symbolizes the multipole polarization of the electron core by the perturbation. This can be written as

$$V' = \sum_{L=1}^{\infty} \left\{ \frac{-1}{R^{L+1}} \right\} \sum_{i=1}^N (r_i)^L P_L(\cos \theta_i) \quad (6.3)$$

$$= \sum_{L=1}^{\infty} (\lambda_L) \sum_{i=1}^N (r_i)^L P_L(\cos \theta_i) \quad (6.4)$$

where

$$\lambda_L = \left\{ \frac{-1}{R^{L+1}} \right\} \quad (6.5)$$

The L-th term in equation (6.4) is responsible for 2^L -pole polarization of the electron core. The 2^L -pole polarizability is defined as $(-1)^{L(L!)}$ times the ratio of the induced 2^L -pole moment to the L-th order gradient of the perturbing potential. The 2^L -pole moment $\mu(2^L\text{-pole})$ is defined as

$$\mu(2^L\text{-pole}) = - \langle \Phi | \sum_{i=1}^N (r_i)^L P_L(\cos \theta_i) | \Phi \rangle \quad (6.6)$$

where Φ represents the total perturbed wave function $(=\Phi_0 + \lambda \Phi')$ for a non-degenerate case in the presence of the perturbation. Here Φ_0 represents the wave function in the absence of any perturbation.

To first-order in λ , the L-th order gradient due to the external point charge q is given by

$$\text{gradient (L-th order)} = (-1)^{L(L!)} \lambda \quad (6.7)$$

Hence the 2^L -pole polarizability $\alpha(2^L\text{-pole})$ can be obtained

using equations (6.6) and (6.7). Thus, we get

$$\alpha(2^L\text{-pole}) = -2 \left\langle \Phi' \left| \sum_{i=1}^N (r_i)^L P_L(\cos \theta_i) \right| \Phi^0 \right\rangle \quad (6.8)$$

As has been said earlier, associated with this 2^L -pole polarizability is a 2^L -pole shielding factor $\gamma(2^L\text{-pole})$. This 2^L -pole shielding factor is defined as the ratio of the change in the L -th order electric field gradient at the site of the nucleus due to the polarized electron core to the L -th order electric field gradient of the perturbing potential alone. Since the electrostatic potential at the nuclear site due to the electron charge distribution is $\sum_{i=1}^N (1/r_i)$, the L -th order derivative of this quantity will give the numerator of $\gamma(2^L\text{-pole})$. Hence we get,

$$\gamma(2^L\text{-pole}) = 2 \left\langle \Phi' \left| \sum_{i=1}^N \frac{P_L(\cos \theta_i)}{(r_i)^{L+1}} \right| \Phi^0 \right\rangle \quad (6.9)$$

In a first-order calculation of $\alpha(2^L\text{-pole})$ or $\gamma(2^L\text{-pole})$ the necessary task is, thus, to evaluate the first order perturbation of the wave function.

Sternheimer and coworkers¹⁻⁸ have examined polarization and shielding effects, first utilizing Thomas-Fermi model of the atom and later adopting the method of direct numerical solution ("perturbation numerical procedure") of the first-order inhomogeneous Schrödinger equation for getting the first-order-perturbation Φ' of the wave function. Ghatikar et al.⁹ have recently adopted a similar procedure for the calculations of the quadrupolar antishielding factors in some rare earth ions.

Das et al.^{10,11} and others¹²⁻¹⁶ treated the first-order inhomogeneous Schrödinger equation by a variational procedure ("perturbation-variation procedure") in which the perturbation of the wave function is obtained analytically by minimizing the second-order energy. Since in this procedure an analytic function is used the labour of numerical integration is avoided. This approach, however, suffers from the problem of maintaining orthogonality¹⁷, self-consistency and inclusion of exchange.

Both the "perturbation-numerical" and the "perturbation-variation" methods are based on the single particle approximation which, just as in the Hartree's SCF method, considers each atomic orbital separately and perturbation in each orbital is determined independently of the perturbation in the other orbitals. In the Hartree-Fock SCF method each one-electron wave function depends on other one-electron wave functions of the system through the exchange and coulomb terms. Likewise, the perturbation in any one-electron wave function should also depend on the perturbations in the rest of the one-electron wave functions. Dalgarno^{17,18}, Kaneko¹⁹ and Allen²⁰ have independently worked out expressions for second-order energy, taking into account the coupling that exists between the various perturbed one-electron wave functions. Dalgarno has shown that the 'perturbation-numerical' and the 'perturbation-variation' methods are approximations to what he calls as "uncoupled HF method". In the 'coupled HF method'^{17,18}, the second-order energy has a number of exchange terms which couple different perturbed one-electron wave functions. Minimization of this energy, maintaining self-consistency, is a cumbersome job, although it yields correct perturbed wave functions. Dalgarno, Kaneko and others have attempted to solve the sets of coupled integro-

therefore been attempted in very simple systems only. Khubchandani et al²¹ started with the second-order energy including exchange terms, but in their variation calculation they subsequently dropped the coupling terms.

The complete Hartree-Fock equation, including the perturbation potential, has been derived and solved by Watson and Freeman²²⁻²⁴ using the unrestricted HF method. Cohen^{25,26} and Cohen and Roothaan²⁷ have also employed a similar procedure of complete solution of the HF equations. In these procedures the effect of the small perturbing potential can be taken care of only by performing the complete HF solution to a very high degree of accuracy. If it is not done so the small effect of the perturbation may be lost giving rise to serious error.

Yoshimine and Hurst²⁸ and Langhoff and Hurst²⁹ have also carried out the calculations of dipole and quadrupole polarizabilities for a large number of two- to twenty-electron atomic systems within the framework of uncoupled HF approximation. Langhoff and Hurst²⁹ have also shown that their procedure is equivalent to the 'perturbation-variation' procedure, provided the latter is carried out under proper orthogonality conditions.

Recently, Lahiri and Mukherji^{30,31} have devised a "self-consistent perturbation" method for obtaining a self-consistent solution by minimizing the second-order energy under fully coupled HF approximation and thus the interdependence of the perturbed one-electron wave functions can be taken into account. The second-order energy minimization is carried out through successive approximations to achieve full self-consistency. As compared to the method employing the complete HF solution this method is better because here the small in the wave function itself

therefore been attempted in very simple systems only. Khubchandani et al²¹ started with the second-order energy including exchange terms, but in their variation calculation they subsequently dropped the coupling terms.

The complete Hartree-Fock equation, including the perturbation potential, has been derived and solved by Watson and Freeman²²⁻²⁴ using the unrestricted HF method. Cohen^{25,26} and Cohen and Roothaan²⁷ have also employed a similar procedure of complete solution of the HF equations. In these procedures the effect of the small perturbing potential can be taken care of only by performing the complete HF solution to a very high degree of accuracy. If it is not done so the small effect of the perturbation may be lost giving rise to serious error.

Yoshimine and Hurst²⁸ and Langhoff and Hurst²⁹ have also carried out the calculations of dipole and quadrupole polarizabilities for a large number of two- to twenty-electron atomic systems within the framework of uncoupled HF approximation. Langhoff and Hurst²⁹ have also shown that their procedure is equivalent to the 'perturbation-variation' procedure, provided the latter is carried out under proper orthogonality conditions.

Recently, Lahiri and Mukherji^{30,31} have devised a "self-consistent perturbation" method for obtaining a self-consistent solution by minimizing the second-order energy under fully coupled HF approximation and thus the interdependence of the perturbed one-electron wave functions can be taken into account. The second-order energy minimization is carried out through successive approximations to achieve full self-consistency. As compared to the method employing the complete HF solution this method is better because here the small perturbation in the wave function itself

is calculated and there is very little chance of error in obtaining this.

In the present work we shall be interested in the theoretical estimates of quadrupole antishielding factors of atoms and ions using Hartree-Fock-Slater wave functions of Herman and Skillman³². Since most frequently one meets with quadrupole antishielding (negative sign of the shielding factor) in atoms and ions we shall refer to the quadrupolar polarizability in this manner. However, there could be cases where the polarizability shielding factor is positive.

It may be mentioned here that many workers³³ have emphasized the marked sensitivity of the multipole polarizabilities to the choice of the unperturbed wave functions. In particular, it has been found that there is marked difference in the results of the calculations using Hartree and Hartree-Fock wave functions due to the fact that the latter includes exchange. The main aim of the present investigation is to test the merits and demerits of the Hartree-Fock-Slater wave functions³² which include the effect of exchange through the Slater free-electron exchange approximation (with a tail correction due to Herman and Skillman³²). In the present calculations of quadrupole antishielding factors starting with the HFS wave functions of Herman and Skillman as the unperturbed wave functions, we shall employ the method of direct numerical solution of the first-order inhomogeneous Schrödinger equation. It may be remarked here that this perturbation-numerical procedure has been used extensively by Sternheimer and hence by using the same procedure it is possible for us to compare our HFS results with his H or HF results for several atoms and ions. It will be worthwhile to compare the results of the calculations made presently with other calculations of the same degree of accuracy

(uncoupled HF approximation) using Hartree and Hartree-Fock wave functions as the unperturbed wave functions. Such a comparison would throw valuable light on the adequacy or otherwise of the HF3 wave functions. For the sake of completeness the results of other calculations will be quoted wherever available.

Electric quadrupole interactions between atomic nuclei and outer electron core have been experimentally investigated in atoms, molecules, metals and salts by a variety of methods such as spin-lattice relaxation measurements in nuclear quadrupole resonance³⁴, dislocation densities measurement by nuclear magnetic resonance³⁵⁻³⁷, ultrasonically induced nuclear magnetic resonance studies³⁸⁻⁴² and Mössbauer effect studies^{43,44}. Interpretation of these experimental observations generally requires a satisfactory model (such as ionic model or covalent model) for the evaluation of the field gradient due to external charges and also a knowledge of the shielding factors. It has been found that none of these models individually gives satisfactory agreement with the theoretical results. Further, it may also be pointed out here that most of the calculations of antishielding factors use free ion unperturbed wave functions. However, the actual fields in which an ion is ^t situated _A definitely changes the free ion unperturbed wave function. It has been found that^{14,29} there is good agreement between experimental and theoretical results using free-ion unperturbed wave function for positive ions but it is not so for negative ions. It seems that the negative ion wave functions are easily deformable by their environment. Contracted unperturbed wave functions have been used by Burns and Wikner¹⁴ to take into account such deformations in negative ions. We shall, however, limit ourselves to the

use of free-ion HFS wave functions.

In section 2, a brief account of the quadrupole antishielding factors χ_{∞} and R will be given. Section 3 will concern itself with a brief description of the procedure for obtaining perturbed wave functions using the method of direct numerical solution of the first-order inhomogeneous differential equation. In that section we also give the details of evaluating χ_{∞} and R factors. In section 4 the results of the present calculations are presented. A discussion of the results obtained is also given.

VI.2 QUADRUPOLE POLARIZATION AND STERNHEIMER ANTISHIELDING FACTORS

The basic quadrupolar Hamiltonian \mathcal{H}_Q for a nucleus with spin I, quadrupole moment Q interacting with an electric field gradient q of axial symmetry has the form

$$\mathcal{H}_Q = \frac{e^2 Q q}{4I(2I-1)} \left[3(I_z)^2 - I(I+1) \right] \quad (6.10)$$

Since, the field gradient is assumed to have axial symmetry we have

$$\left. \begin{aligned} V_{zz} &= eq \\ \text{and } \eta &= \frac{V_{xx} - V_{yy}}{V_{zz}} = 0 \end{aligned} \right\} \quad (6.11)$$

Two types of "source field gradients" q are usually considered. Firstly, a field gradient q_{lat} will be produced due to the lattice charges (or crystalline field). Secondly, in an atom or ion having a valence electron in a non-spherical orbital a field gradient q_{val} at the site of

the nucleus will be produced by this electron. Hence, in the simplest way one can think that q of equation (6.10) is given by $q = q_{\text{val}} + q_{\text{lat}}$. But this is not entirely correct. In view of the discussion presented in section 1 we now know that the presence of an external charge, for example, produces multipole polarization due to perturbation of spherical electronic core of an atom or ion. We are interested here only in the quadrupole polarization of the core due to both external charges and the valence electron in a non-spherical orbital. In general, in the presence of a source field gradient, an induced quadrupole polarization of the electron core takes place. Such a distortion in turn gives rise to additional (induced) electric field gradient which is sometimes several orders of magnitude higher than the source field gradient. In view of this effect, q of equation (6.10) should be actually written as

$$q = q_{\text{val}} (1-R) + q_{\text{lat}} (1-\chi_{\infty}) \quad (6.12)$$

where it has been assumed that $Rq_{\text{val}} (= q_{\text{val}}^{\text{ind}})$ and $\chi_{\infty}q_{\text{lat}} (= q_{\text{lat}}^{\text{ind}})$ are the induced electric field gradients produced at the nuclear site by the distortions in the electron core of the atom or ion due to q_{val} and q_{lat} respectively and that these induced electric field gradients oppose (conventionally) the respective source electric field gradients. The proportionality factors R and χ_{∞} are called Sternheimer antishielding factors.

VI.3 CALCULATION OF QUADRUPOLE POLARIZATION EFFECTS BY 'PERTURBATION-NUMERICAL' METHOD

For $L = 2$ equation (6.4) gives the perturbing potential responsible for quadrupole polarization of the electron core of an atom

or ion due to a charge of 1 a.u., i.e. the electric field gradient produced by this charge, when it is completely outside the atom or ion at a distance R from the nucleus. Thus, for a particular electron of the atom or ion at a position (r, θ, ϕ) with respect to the nucleus the perturbing Hamiltonian \mathcal{H}_1 is given by

$$\mathcal{H}_1 = \frac{-(3 \cos^2 \theta - 1) r^2}{2(R)^3} \quad (6.13)$$

Here atomic units have been used. The zero-order Hamiltonian \mathcal{H}_0 of the electron is given by

$$\mathcal{H}_0 = -\frac{1}{2} \nabla^2 + V_0 \quad (6.14)$$

Now, if Ψ_0 and Ψ_1 represent the zero-order wave function and its perturbation, respectively, we have the equation

$$(\mathcal{H}_0 - E_0) \Psi_1 = -(\mathcal{H}_1 - E_1) \Psi_0 \quad (6.15)$$

which is the second-order perturbation relation. Here

$$\left. \begin{aligned} \langle \Psi_0 | \Psi_1 \rangle &= 0 \\ E_0 &= \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle \\ \text{and } E_1 &= \langle \Psi_0 | \mathcal{H}_1 | \Psi_0 \rangle \end{aligned} \right\} \quad (6.16)$$

Using equations of the type (6.15) one can calculate the electronic distortions due to the source electric field gradient. The calculation of the interaction of this induced quadrupole moment of the electron core with the nuclear quadrupole moment would be the second step.

An alternative approach would be to calculate, first, the electronic distortion of the core due to Q , the nuclear quadrupole moment and then the interaction of this distortion with the source field gradient in question. Both these approaches will give the same result in the second order perturbation theory¹⁸. The latter approach has been employed by Sternheimer in his perturbation-numerical calculations. In this case the perturbing Hamiltonian \mathcal{H}_1 of equation (6.15) will be given by

$$\mathcal{H}_1 = \frac{-Q(3 \cos^2 \theta - 1)}{2(r)^3} \quad (6.17)$$

in Rydberg units; here Q and r are expressed in a_H^2 and a_H units respectively, r and θ being the length of the radius vector from the nucleus and the angle included by this vector and the axis of the nuclear quadrupole moment Q .

Since the quadrupolar perturbing Hamiltonian \mathcal{H}_1 has $Y_2^0(\theta, \phi)$ symmetry, the perturbed wave function will have mixed with it the unperturbed wave function character so that

$$\left. \begin{aligned} \psi_0 (l=0) &\longrightarrow N_0 \left\{ \psi_0(l=0) + \psi_1(l=2) \right\} \\ \psi_0 (l=1) &\longrightarrow N_1 \left\{ \psi_0(l=1) + \psi_1(l=1) + \psi_1(l=3) \right\} \\ \psi_0 (l>1) &\longrightarrow N_1 \left\{ \psi_0(l) + \psi_1(l) + \psi_1(l+2) + \psi_1(l-2) \right\} \end{aligned} \right\} \quad (6.18)$$

where N 's represent the normalization constants. The mixing of ψ_0 and ψ_1 having same 'l' value is called a "radial" excitation whereas the

mixing of ψ_0 and ψ_1 having different 'l' values is called "angular" excitation.

We may take the unperturbed function and its perturbation as ψ_0 and ψ_1 for an excitation $l \rightarrow l'$ as

$$\left. \begin{aligned} \psi_0 &= \frac{u_0(r)}{r} \Theta_0(\theta, \phi) \\ \psi_1 &= \frac{u_1(r)}{r} \Theta_1(\theta, \phi) \end{aligned} \right\} \quad (6.19)$$

where u_0 and u_1 represent r times the unperturbed radial wave function and its perturbation. The unperturbed function $u_0(r)$ is normalised to unity in the following manner:

$$\int_0^{\infty} \{u_0(r)\}^2 dr = 1 \quad (6.20)$$

and according to the first equation in the set of equations (6.16) we must have for all the radial ($nl \rightarrow l$) excitations

$$\int_0^{\infty} u_0(r) u_1(r) dr = 0 \quad (6.21)$$

We note that (i) the first order perturbation energy is given by equation (6.16) and (ii) ψ_1 will have an additional angular dependence ($3\cos^2\theta - 1$) and hence we can perform a separation of the variables in equation (6.15) which would then take the form:

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{(r)^2} + V_0 - E_0 \right] u_1 = \left[\frac{1}{(r)^3} - \left\langle \frac{1}{(r)^3} \right\rangle \delta_{ll'} \right] u_0 \quad (6.22)$$

where $\langle 1/r^3 \rangle$ is the average of $1/r^3$ over the unperturbed function $u_0(r)$. Since we have

$$V_0 - E_0 = \frac{1}{u_0} \frac{d^2 u_0}{dr^2} - \frac{l(l+1)}{r^2} \quad (6.23)$$

equation (6.22) takes the form

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1) - l(l+1)}{r^2} + \frac{1}{u_0} \frac{d^2 u_0}{dr^2} \right] u_1 = u_0 \left[\frac{1}{(r)^3} - \left\langle \frac{1}{(r)^3} \right\rangle \delta_{ll'} \right] \quad (6.24)$$

It is this equation which is actually solved numerically for various excitations $l(u_0) \rightarrow l'(u_1)$ in Sternheimer's "perturbation-numerical" approach. As mentioned earlier, we shall also be using this procedure for the present calculations of V_∞ and R factors.

The factor V_∞ for the various excitations are given by

$$V_\infty (nl \rightarrow l') = C(l \rightarrow l') \int_0^\infty u_0(r) u_1(r) r^2 dr \quad (6.25)$$

where the coefficients $C(l \rightarrow l')$ represent the effect of the integrations over the angular variables with the summation over magnetic substates.

For closed-shells we have

$$\left. \begin{aligned} C(s \rightarrow d) &= C(d \rightarrow s) = 8/5 \\ C(p \rightarrow p) &= 48/25 \\ C(p \rightarrow f) &= C(f \rightarrow p) = 72/25 \\ C(d \rightarrow d) &= 16/7 \\ C(d \rightarrow g) &= C(g \rightarrow d) = 144/35 \\ C(f \rightarrow f) &= 224/75 \end{aligned} \right\} \quad (6.26)$$

The R factor for the various excitations is given by

$R(nl \rightarrow l')$

$$= C(1 \rightarrow 1') \frac{\int_0^\infty u_{\text{val}}^2(r_c) \left[\int_0^{r_c} u_0(r) u_1(r) r^2 dr + (r_c)^5 \int_{r_c}^\infty u_0(r) u_1(r) \frac{1}{r^3} dr \right] \frac{dr_c}{(r_c)^3}}{\int_0^\infty u_{\text{val}}^2(r_c) \frac{1}{(r_c)^3} dr_c} \quad (6.27)$$

where $u_{\text{val}}(r)$ represents r times the radial part of the valence electron unperturbed wave function and the constants $C(1 \rightarrow 1')$ have the same meaning as those in equation (6.25).

VI.4 PROCEDURE ADOPTED FOR NUMERICAL SOLUTIONS FOR PERTURBATIONS $u_0(1) \rightarrow u_1(1')$

Equation (6.24) has been solved numerically employing the method of finite differences⁴⁵⁻⁴⁷. Replacing all second derivatives of equation (6.24) by second-order differences we obtain for inward and outward integration the following equation

$$\begin{aligned} - \left[\frac{u_1(r+\delta r) - 2u_1(r) + u_1(r-\delta r)}{(\delta r)^2} \right] + \left[\frac{l'(l'+1) - l(l+1)}{(r)^2} \right] u_1(r) \\ + \frac{u_1(r)}{u_0(r)} \left[\frac{u_0(r+\delta r) - 2u_0(r) + u_0(r-\delta r)}{(\delta r)^2} \right] \\ = u_0(r) \left[\frac{1}{(r)^3} - \left\langle \frac{1}{(r)^3} \right\rangle \delta_{11'} \right] \end{aligned} \quad (6.28)$$

If we assume that the points $(r+\delta r)$, r and $(r-\delta r)$ correspond to the $(J+1)$ -th, J -th and $(J-1)$ -th points of the integration mesh, equation (6.28) can be rewritten as

$$\begin{aligned}
 & u_1(J+1) \\
 &= u_1(J) \left[2 + (\delta r)^2 \frac{l'(l'+1) - l(l+1)}{(r(J))^2} + \frac{u_o(J+1) - 2u_o(J) + u_o(J-1)}{u_o(J)} \right] \\
 &\quad - u_1(J-1) - u_o(J) (\delta r)^2 \left[\frac{1}{(r(J))^3} - \left\langle \frac{1}{r^3} \right\rangle \delta_{ll'} \right]
 \end{aligned}
 \tag{6.29}$$

If the values of the perturbation u_1 of the wave function are known for two or more innermost points, for example the points $J = 1$ and $J = 2$, the above equation can be employed for successive outward integration. Similarly, if the values of the perturbation u_1 are known for two or more outermost points, for example the points $J = J_{\text{last}}$ and $J = J_{\text{last}} - 1$, this equation can be employed for successive inward integration.

For each excitation $l \rightarrow l'$, whether angular ($l \neq l'$) or radial ($l = l'$), we have performed one outward integration and one inward integration of equation (6.29) and matched the two solutions at an intermediate radius $r \approx 0.1$ a.u. It is assumed that for the outward integration the perturbation u_1 at the various mesh points (J 's) is given by

$$u_1(J) = A C(J) + B(J) \tag{6.30}$$

where A is a constant and $C(J)$ and $B(J)$ are certain numerical quantities pertaining to the J -th mesh point. It can easily be seen that knowing

the values of $C(J)$ and $B(J)$ at two or more points near the nucleus the outward integration of equation (6.29) can be performed and solution u_1 obtained at various mesh points in the form (6.30). However, A is to be determined by matching this solution with that obtained by an inward integration.

For the inward integration it has been assumed that the perturbation u_1 is obtainable in the form

$$u_1(J) = a E(J) + D(J) \quad (6.31)$$

at the various mesh points (J 's). Just as in the case of the outward integration (see eqn. 6.30) here also ' a ' is an unknown constant and $E(J)$ and $D(J)$ are certain numerical quantities pertaining to the J -th mesh point. The inward integration can be performed and the values of $E(J)$ and $D(J)$ at the various mesh points can be obtained provided $E(J)$ and $D(J)$ are known at least at two outermost points near the tail of the unperturbed function u_0 .

The boundary conditions near the nucleus and those near the tail of the unperturbed wave function u_0 are utilized to obtain the necessary values of $C(J)$ and $B(J)$ and $E(J)$ and $D(J)$ respectively for starting the outward and inward integrations of equation (6.29).

Thus, after performing the outward and inward integrations we obtain the values of $C(J)$, $B(J)$ and $E(J)$, $D(J)$ for all the mesh points. The values of the constants ' A ' and ' a ' are determined by employing the conditions of the continuity of the function u_1 and its first derivative at the matching radius.

We shall now describe the various excitations and the boundary conditions employed in their solutions one by one.

(A) For Radial ($l = l'$) Excitations

In this case equation (6.29) takes the form

$$\begin{aligned}
 u_1(J+1) &= u_1(J) \left[2 + \frac{u_0(J+1) - 2u_0(J) + u_0(J-1)}{u_0(J)} \right] \\
 &\quad - u_1(J-1) - u_0(J) (\nabla r)^2 \left[\frac{1}{(r(J))^3} - \left\langle \frac{1}{r^3} \right\rangle \right]
 \end{aligned} \tag{6.32}$$

for all radial excitations.

For sufficiently small r values both the unperturbed function u_0 and its perturbation u_1 can be obtained by the first term of the polynomials into which these can be expanded near the nucleus. Hence, for the excitation ($nl \rightarrow l$) we have

$$u_1(r \text{ small}) = A \cdot (r)^1 \tag{6.33}$$

and hence we set

$$\left. \begin{aligned}
 B(1) &= 0 & C(1) &= \{r(1)\}^{(1)} \\
 & & &= 0 \text{ (since } r(1) = 0) \\
 B(2) &= 0 & C(2) &= \{r(2)\}^{(1)} \\
 B(3) &= 0 & C(3) &= \{r(3)\}^{(1)}
 \end{aligned} \right\} \tag{6.34}$$

and then perform the outward integration of equation (6.32) to obtain

B(4), C(4); B(5), C(5); etc. From equation (6.29) it also follows that for sufficiently large values of r the unperturbed function u_0 and the perturbation u_1 are related as

$$u_1(r \text{ large}) = a u_0(r \text{ large}) \quad (6.35)$$

and therefore the inward integration of equation (6.32) has been carried out using the following tail boundary conditions

$$\left. \begin{aligned} D(J_{\text{last}}) &= E(J_{\text{last}}) = u_0(J_{\text{last}}) \\ D(J_{\text{last}}^{-1}) &= E(J_{\text{last}}^{-1}) = u_0(J_{\text{last}}^{-1}) \\ D(J_{\text{last}}^{-2}) &= E(J_{\text{last}}^{-2}) = u_0(J_{\text{last}}^{-2}) \end{aligned} \right\} \quad (6.36)$$

As has been said earlier these two solutions are then matched at the matching radius $r \approx 0.1$ a.u. Finally, the perturbation u_1 is made orthogonal to the unperturbed function u_0 (c.f. eqn. 6.21) by adding $-Su_0$ to u_1 , where $S = \int_0^{\infty} u_0 u_1 dr$.

(B) For Angular ($l \neq l'$) Excitations

In these cases equation (6.29) reduces to the following form

$$\begin{aligned} u_1(J+1) &= u_1(J) \left[2 + (\delta r)^2 \frac{\Delta 1}{(r(J))^2} + \frac{u_0(J+1) - 2u_0(J) + u_0(J-1)}{u_0(J)} \right] \\ &\quad - u_1(J-1) - u_0(J) (\delta r)^2 \frac{1}{(r(J))^3} \end{aligned}$$

(6.37)

where Δl is defined as

$$\Delta l = l'(l'+1) - l(l+1) \quad (6.38)$$

We shall now take one by one those angular excitations which are of interest to us and describe the process of outward integration of the corresponding equation (6.37).

(B.1) Angular Excitation $s \rightarrow d$ ($l = 0 \rightarrow l' = 2$)

The perturbation u_1 in this case has finite value at the origin and this is given by

$$u_1(0) = \frac{a_0}{l'(l'+1)} = \frac{a_0}{6} \quad (6.39)$$

where a_0 is the coefficient of the first term of the polynomial into which u_0 can be expressed near the origin so that

$$a_0 = \left| \frac{u_0(ns)}{r} \right|_{r \rightarrow 0} \quad (6.40)$$

Also, near the origin we have

$$u_1(r \text{ small}) = A'r \quad (6.41)$$

where A' is a constant. Therefore, for the outward integration of the corresponding equation (6.37) we use the following initial conditions.

$$\left. \begin{array}{ll} C(1) = 0 & B(1) = a_0/6 \\ C(2) = -r(2) & B(2) = B(1) \\ C(3) = -r(3) & B(3) = B(1) \\ C(4) = -r(4) & B(4) = B(1) \end{array} \right\} \quad (6.42)$$

(B.2) Angular Excitation p \rightarrow f ($l = 1 \rightarrow l' = 3$)

In this case the perturbation u_1 is zero at the origin.

However, near the origin it behaves as

$$u_1(r \text{ small}) = \frac{b_o r}{1'(1'+1)} = \frac{b_o r}{12} \quad (6.43)$$

where b_o is the coefficient of the first term of the polynomial into which the unperturbed function u_o can be expressed near the origin. Thus

$$b_o = \left| \frac{u_o(np)}{r^2} \right|_{r \rightarrow 0} \quad (6.44)$$

The boundary conditions used here for the outward integration of equation (6.37) are therefore set as

$$\left. \begin{aligned} C(1) &= 0 & B(1) &= \frac{b_o r(1)}{12} \\ & & &= 0 \text{ (since } r(1)=0) \\ C(2) &= r(2) & B(2) &= \frac{b_o r(2)}{12} \\ C(3) &= r(3) & B(3) &= \frac{b_o r(3)}{12} \\ C(4) &= r(4) & B(4) &= \frac{b_o r(4)}{12} \end{aligned} \right\} \quad (6.45)$$

(B.3) Angular Excitation d \rightarrow g ($l = 2 \rightarrow l' = 4$)

In this case also the perturbation u_1 is zero at the origin.

Near the origin, it however, behaves as

$$u_1(r) = \frac{c_o r^2}{1'(1'+1)} \quad (6.46)$$

where c_0 is the first term of the polynomial into which the unperturbed function u_0/r^3 can be expressed near the origin i.e.

$$c_0 = \left| \frac{u_0(r)}{r^3} \right|_{r \rightarrow 0} \quad (6.47)$$

Hence, one can take the following values of $C(J)$ and $B(J)$ at and near the origin to start the outward integration of equation (6.37).

$$\left. \begin{aligned} C(1) &= 0 & B(1) &= 0 \\ C(2) &= \{r(2)\}^2 & B(2) &= \frac{c_0 \{r(2)\}^2}{20} \\ C(3) &= \{r(3)\}^2 & B(3) &= \frac{c_0 \{r(3)\}^2}{20} \end{aligned} \right\} \quad (6.48)$$

(B.4) Angular Excitation $d \rightarrow s$ ($l = 2 \rightarrow l' = 0$)

The perturbation u_1 will be zero at the origin and if we assume that the unperturbed function u_0 near the origin is given by

$$u_0(r) = \frac{c_0(r)^3 + c_1(r)^4 + c_2(r)^5 + \dots}{r^3} \quad (6.49)$$

we can see by inserting this form of u_0 in equation (6.37) with $\Delta l = -6$, that the perturbation u_1 near the origin behaves as

$$\begin{aligned} u_1(r) &= \frac{(c_0)^2 r}{2c_1(1)(1+1)} \\ &= \frac{(c_0)^2 r}{12 c_1} \end{aligned} \quad (6.50)$$

Thus, for the outward integration of equation (6.37) in this case we start with

$$\left. \begin{aligned}
 C(1) &= 0 & B(1) &= 0 \\
 C(2) &= r(2) & B(2) &= \frac{(c_0)^2}{12c_1} r(2) \\
 C(3) &= r(3) & B(3) &= \frac{(c_0)^2}{12c_1} r(3) \\
 C(4) &= r(4) & B(4) &= \frac{(c_0)^2}{12c_1} r(4)
 \end{aligned} \right\} \quad (6.51)$$

As regards the ~~inward~~ integration process adopted here for equation (6.37), it may be remarked that this is done exactly in the same way as that adopted for the inward ~~integration~~ of equation (6.32) which corresponds to the radial excitations.

The solutions of the outward and inward integrations are finally matched ~~at~~ the intermediate radius and constants A (see eqn. (6.30)) and a (see eqn. (6.31)) are determined exactly in the same manner as that followed for the radial excitations.

One should note here that in the case of angular excitations u_1 and u_0 are already orthogonal and so it is not necessary to again make u_1 orthogonal to u_0 .

VI.5 CERTAIN REMARKS ON THE PROCEDURE OF NUMERICAL SOLUTION ADOPTED

In the previous section a description of the procedure for the

numerical integrations of the inhomogeneous Schrödinger equation was presented. The following points may be noted about this procedure.

- (i) We have always performed only one outward and only one inward integration and matched the two solutions at the matching radius. It has been found that although this procedure seems to work well for radial excitations, it is not equally good for angular excitations. In the latter case it will be better if one performs several outward integrations by numerically varying the constant A (see eqn. (6.30)) till the solution becomes exponentially decaying in the outer region and then matches the outward and inward integration solutions to find out the constant a .
- (ii) The boundary conditions taken near the nucleus are not very stringent. These can be made more stringent and the results improved. However, it is believed that the alterations in the results due to such changes in the starting conditions will not be significant.
- (iii) As has been said in remark (i) the use of a single outward and a single inward integration is not suitable for the angular excitations. It is more so in the case of the angular excitation $nd \rightarrow s$ which corresponds to $\Delta l = -6$ (see equation (6.38)). It can be easily seen that in all other angular excitations Δl remains positive. The effect of this fact is that u_1 and u_0 happen to have the same number of nodes in all the excitations considered presently excepting in the excitation $nd \rightarrow s$. Actually u_1 ($nd \rightarrow s$)

has one more node than the corresponding unperturbed function $u_0(nd)$. Due to this behaviour of the solutions of the perturbations $u_1(nd \rightarrow s)$, the procedure described in section 4 is not reliable for this case. This point has also been noted by Sternheimer⁴⁸ who has found that for $(nd \rightarrow s)$ excitations (Δl being negative) the inward integration of equation (6.37) is very unstable. For example, a very small error in u_1 at large r (of the order of one part in 10^5 to 10^6) will lead to a function which diverges near the nucleus. Hence, in the case of $(nd \rightarrow s)$ excitations one has to be careful both for the outward and inward integrations. It is therefore advisable to perform several outward and several inward integrations in this case and match the two well-behaved solutions at the intermediate radius.

In view of the above remarks one may note that the values of the antishielding factor γ_∞ calculated here are reliable because the contributions to this factor from the angular excitations is very small as compared to that from the radial excitations. On the otherhand, the values of the R factor will be affected. Work on the modifications of our existing computer program to take into account the three points mentioned in the preceding paragraph is in progress.

Before coming to the results and their discussion it may be pointed out here that the HFS wave functions³² are available as X vs $P(X)$ tables where X is the variable appearing in the Thomas-Fermi model of the

atom and is related to the variable r as

$$r = \mu X \quad (6.52)$$

μ in this equation is the parameter defined as

$$\mu = \left(\frac{1}{2}\right) (3\pi/4)^{\left(\frac{2}{3}\right)} (Z)^{\left(-\frac{1}{3}\right)} \quad (6.53)$$

Hence in view of the above fact, instead of r the variable X is used in our computer program. All the expressions which are used in our program have therefore been modified accordingly.

VI.6 RESULTS AND DISCUSSION

The results of calculations of $\gamma_{\infty}(nl \rightarrow 1')$ contributions and total γ_{∞} in the systems Al^{+++} , Cl^{-} , Pr^{+++} , Tm^{+++} , Ce^{+++} , Na^{+} , In^{+++} , Y^{+++} , Bi^{+++} and Am^{++} are presented in Tables VI. 1 to VI. 8. The results of $R(nl \rightarrow 1')$ factor calculations in the rare earth ions Pr^{+++} , Tm^{+++} and Ce^{+++} are given in Table VI. 9. A comparison of the present results with those obtained from other wave functions is also given. The results obtained by using the perturbation-variation approach and other methods are also indicated.

As has been said earlier the method employed in the present investigation for the numerical integration of the Schrödinger equation is well-suited for the radial excitations only. Further, major contribution to γ_{∞} comes from the radial excitations only whereas for the R factor calculations, the contributions from both radial and angular excitations are important. Thus, it is believed that the γ_{∞} results of the present investigation are more reliable than the R factor results.

The aim of the present work is, however, to see how the Hartree-Fock-Slater wave functions compare with the Hartree and Hartree-Fock wave functions as regards their capability of reproducing the quadrupole antishielding factors. In view of the earlier discussion, we shall restrict ourselves to a comparison of our χ_{∞} values with those calculated using Hartree or Hartree-Fock wave functions. Furthermore, from the present point of view, it would be most reasonable to compare the results of our investigation with the results of other calculations which employ the same method as employed here, namely the perturbation-numerical method. The "perturbation-variation method" is, however, more or less of the same degree of accuracy as the perturbation-numerical method employed here. Hence, occasionally we shall also utilize these results for comparison. The rest of the methods take into account, in some way or the other, the interdependence of the perturbed single-electron orbitals and hence they are of greater degree of accuracy.

In Tables VI.1 and VI.2 we have included the results of the perturbation-variation calculations of χ_{∞} factors for Al^{+++} and Cl^{-} made by Burns¹³ using both the Hartree^{49,50} and Hartree-Fock^{51,52} wave functions. These results clearly indicate that the effect of including exchange in the unperturbed wave functions is to bring down the value of $|\chi_{\infty}|$. This effect has been confirmed by several other workers also. For example, Sternheimer⁷, from calculations on Cs^{+} and Rb^{+} employing his perturbation-numerical approach finds a similar effect. This is reasonable also, because exchange contracts the outermost part of the electron density which in turn affects the contributions of the outer orbitals to χ_{∞} in the above manner. It must be noted in this connection

TABLE VI.1

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Al^{+++}

Distortion	Present Perturbation -Numerical Calculation	Other Calculations		
		Perturbation -Numerical	Perturbation -Variation	Other Methods
1	2	3	4	5
$1s \rightarrow nd$	0.0539	0.0530 ^a	0.031 ^b	0.04836 ^c
$2s \rightarrow nd$	0.1740	0.1744 ^a	0.278 ^b	0.31180 ^c
			0.2775 ^{d1}	
			0.2652 ^{d2}	
$2p \rightarrow np$	-2.8908	-2.8210 ^a	-3.129 ^b	
			-3.258 ^{d1}	
			-2.837 ^{d2}	
$2p \rightarrow nf$	0.2290	0.2350 ^a	0.230 ^b	-2.596 ^c ($2p \rightarrow nf+np$)
			0.2392 ^{d1}	
			0.2311 ^{d2}	
Total Angular	0.4563	0.463 ^a		
Total Radial	-2.8908	-2.8210 ^a		
Total	-2.4339	-2.358 ^a	-2.590 ^b	-2.236 ^c
				-2.570 ^e

a) Calculated by Sternheimer (ref. 7) using Hartree-Fock wave functions of Froese (ref. 51). The contribution from $1s \rightarrow nd$ excitation was, however, obtained by using hydrogenic wave functions.

-Contd.

Table VI.1 (Continued)

- b) Calculated by Das and Bersohn (ref. 10) using analytic HF wave functions interpolated by Lowdin (ref. 53).
- c) Calculated by Langhoff and Hurst (ref. 29) within the framework of an uncoupled HF approximation, subject to proviso that exchange part of the Fock potential be expressable as a multiplicative function. The wave function used is HF function of Clementi (ref. 57)
- d) Calculated by Burns (ref. 13). d1 and d2 correspond to the use of Hartree (ref. 49) and Hartree-Fock (ref. 51) wave functions respectively.
- e) Calculated by Lahiri and Mukherji (ref. 31) following their self-consistent perturbation method (ref. 30). The result is accurate in the coupled HF scheme.

TABLE VI.2

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Cl^-

Distortion	Present Perturbation -Numerical Calculation	Other Calculations		
		Perturbation -Numerical	Perturbation -Variation	Other Methods
1	2	3	4	5
$1s \rightarrow nd$	0.0411			0.1379^{a1} 0.0453^{a2}
$2s \rightarrow nd$	0.1179		0.1996^{b1} 0.1951^{b2}	0.1924^{a1} 0.2115^{a2}
$2p \rightarrow np$	-1.5372	-1.5^c -1.51^d	-1.643^{b1} -1.522^{b2} -1.030^e	-12.1^f
$2p \rightarrow nf$	0.1563		0.1602^{b1} 0.1586^{b2}	-0.5317^{a1} ($2p \rightarrow np+nf$) -1.006^{a2} ($2p \rightarrow np+nf$)
$3s \rightarrow nd$	0.3833		0.6765^{b1} 0.6343^{b2}	-0.7659^{a1} -0.7857^{a2}
$3p \rightarrow np$	-81.8744	-56.5^c -57.0^d -68.4^g	-158.49^{b1} -50.07^{b2} -49.95^e -158.5^h -50.07^h -27.04^h	-78.3^f

Table VI.2 (Continued)

1	2	3	4	5
$3p \rightarrow nf$	0.7016		0.7351^{b1}	-67.13^{a1} ($3p \rightarrow np+nf$)
			0.7361^{b2}	-53.95^{a2} ($3p \rightarrow np+nf$)
Total Angular	1.4002	1.42^c 1.4^d	1.7^e	$3.4-5.5^f$
Total Radial	-83.4116	-58.00^c -58.51^d		
Total	-82.0114	-56.2^c -57.11^d	-49.28^e	-66.56^{a1} -53.91^{a2} $-87.0 \text{ to } -84.9^f$ -63.21^i

- a) Calculated by Langhoff and Hurst (ref. 29) within the framework of an uncoupled HF approximation, subject to proviso that exchange part of the Fock potential be expressible as a multiplicative function. $a1$ and $a2$ correspond to the use of HF functions of Watson and Freeman (ref. 22) and Clementi et al. (ref. 58).
- b) Calculated by Burns (ref. 13). $b1$ and $b2$ correspond to the use of Hartree and Hartree-Fock functions of Hartree (ref. 50) and Hartree and Hartree (ref. 52) respectively.
- c) Calculated by Sternheimer and Foley (ref. 5) using Hartree-Fock function of Hartree and Hartree (ref. 52). Total angular contribution was, however, calculated earlier by Foley et al. (ref. 3) using these Hartree-Fock functions.
- d) Calculated recently by Sternheimer (ref. 7) using Hartree-Fock functions of Hartree and Hartree (ref. 52). In this work Sternheimer also found that the effect of taking into account the direct (non-exchange) terms of the electrostatic interaction in second order is to change the value from -57.11 to -45.9 .

-Contd.

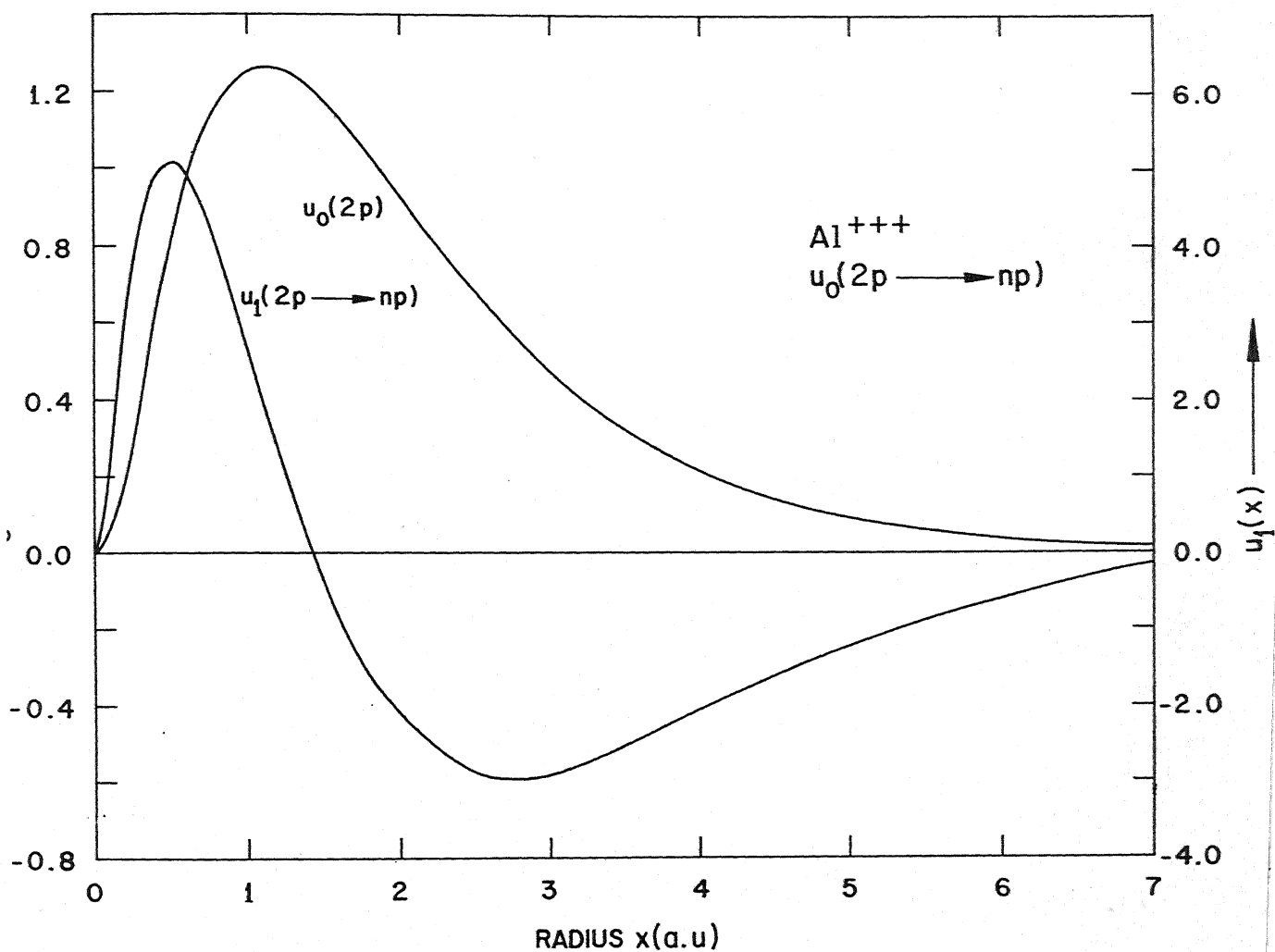
Table VI.2 (Continued)

- e) Calculated by Wickner and Das (ref. 11) using Hartree-Fock functions of Hartree and Hartree (ref. 52). The total angular contribution +1.7 is, however, estimated using Thomas-Fermi model of the atom. These authors also calculated the total angular contribution of +1.40 using the perturbation-variation procedure.
- f) Calculated by Watson and Freeman (ref. 22) using their self-consistent field UHF method.
- g) Calculated recently by Sternheimer (ref. 7) using Hartree-Fock function of Watson and Freeman (ref. 22).
- h) Calculated by Burns and Wickner (ref. 14). Values -158.5 and -50.07 correspond to the use of Hartree and Hartree-Fock functions of Hartree (ref. 50) and Hartree and Hartree (ref. 52) respectively. The value -27.07 is obtained by taking into account the contraction of the Hartree-Fock wave function of Hartree and Hartree (ref. 52) due to the actual fields in which the ion is situated.
- i) Calculated by Lahiri and Mukherji (ref. 31) following their self-consistent perturbation procedure (ref. 30). The result is accurate in coupled HF scheme.

that the outer orbitals contribute the most to γ_{∞} in contrast to the inner orbitals.

The results of γ_{∞} ($nl \rightarrow l'$) and total γ_{∞} for Al^{+++} calculated presently (see Table VI.1) compare very well with those calculated by Sternheimer⁷ using Hartree-Fock wave functions of Froese⁵¹ indicating thereby the fact that HFS wave functions are pretty good approximation to HF wave functions. A value of γ_{∞} (total) = -2.590 was calculated by Das and Bersohn¹⁰ earlier using the analytic HF wave functions interpolated by Lowdin⁵³. Lowdin's wave functions thus seem to be somewhat more external than the HF wave functions of Froese⁵¹ which result in the value -2.358 for γ_{∞} (total). The HFS value γ_{∞} (total) = -2.434, however, indicates the fact that the HFS wave functions are slightly external than the HF wave functions. The fact is confirmed further when we compare the γ_{∞} ($2p \rightarrow np$) value of the present calculation with that of Sternheimer's³ calculations. In passing it may be mentioned here that Sternheimer¹ has carried out R factor calculation on Al^{+++} explicitly including the exchange terms in the interaction energy with the induced quadrupole moment for various orbital electrons. This procedure, however, has not been used widely in the literature. As an example of the present calculations of the perturbations in Al^{+++} , Figure VI.1 shows the perturbation $u_1(2p \rightarrow np)_{HFS}$ together with the unperturbed $u_0(2p)_{HFS}$ function.

In Table VI.2, which presents our HFS results of γ_{∞} calculations for Cl^- , we have also included a result from perturbation-variation calculation of γ_{∞} ($3p \rightarrow np$) carried out by Burns and Wickner¹⁴ utilizing Hartree function⁵⁰. The absolute value of γ_{∞} ($3p \rightarrow np$) = 158.5 obtained with Hartree wave function is much larger than other



VI.1: THE 2p HFS FUNCTION $u_0(2p)$ AND ITS PERTURBATION $u_1(2p \rightarrow np)$ FOR Al^{+++} . THE RIGHT-HAND ORDINATE SCALE PERTAINS TO u_1 ; THE LEFT-HAND ORDINATE SCALE PERTAINS TO u_0 .

values calculated using Hartree-Fock wave functions (vide Table VI.2). The $\left| \gamma_{\infty}(3p \rightarrow np) \right|_{\text{HF}}$ values calculated in the perturbation-numerical approach ranges from 56.5 to 68.4. The value obtained using the HFS wave functions, however, corresponds to $\left| \gamma_{\infty}(3p \rightarrow np) \right| = 81.874$. This indicates the fact that for the negative ions, the difference between HFS and HF wave functions is larger than that for the positive ions. Further, it is surprising that the $\gamma_{\infty}(\text{total})$ for Cl^- obtained by us using HFS wave functions compare most favourably with the value obtained by Watson and Freeman²² following their self-consistent field UHF-method. Figure VI.2 shows the unperturbed $u_0(1s)_{\text{HFS}}$ function and the corresponding $u_1(1s \rightarrow nd)_{\text{HFS}}$ perturbation and Figure VI.3 shows the unperturbed $u_0(3p)_{\text{HFS}}$ function and the corresponding $u_1(3p \rightarrow np)_{\text{HFS}}$ perturbation for Cl^- ion.

In Tables VI.3, VI.4 and VI.5 the results for $\gamma_{\infty}(nl \rightarrow 1')$ and total γ_{∞} for the rare earth ions Pr^{+++} , Tm^{+++} and Ce^{+++} have been presented. From Tables VI.3 and VI.4 we clearly see that the use of the HFS wave functions in our calculations brings down the $\left| \gamma_{\infty}(\text{total}) \right|$ values as compared to those calculated by Sternheimer^{6,7} and by Ghatikar et al.⁹ Both these groups utilized the Hartree functions of Ridley⁵⁴. No results of calculations utilizing HF wave functions as the unperturbed ones exist because of the lack of the Hartree-Fock functions for Pr^{+++} and Tm^{+++} ions. For Ce^{+++} (see Table VI.5) we find that our results for the outer orbital contributions to $\gamma_{\infty}(\text{total})$ compare favourably with those of Freeman and Watson²³ who performed complete m_l -UHF solution of the Hartree-Fock equation including the perturbation potential. This method is believed to be more accurate than the one employed by us since this is an

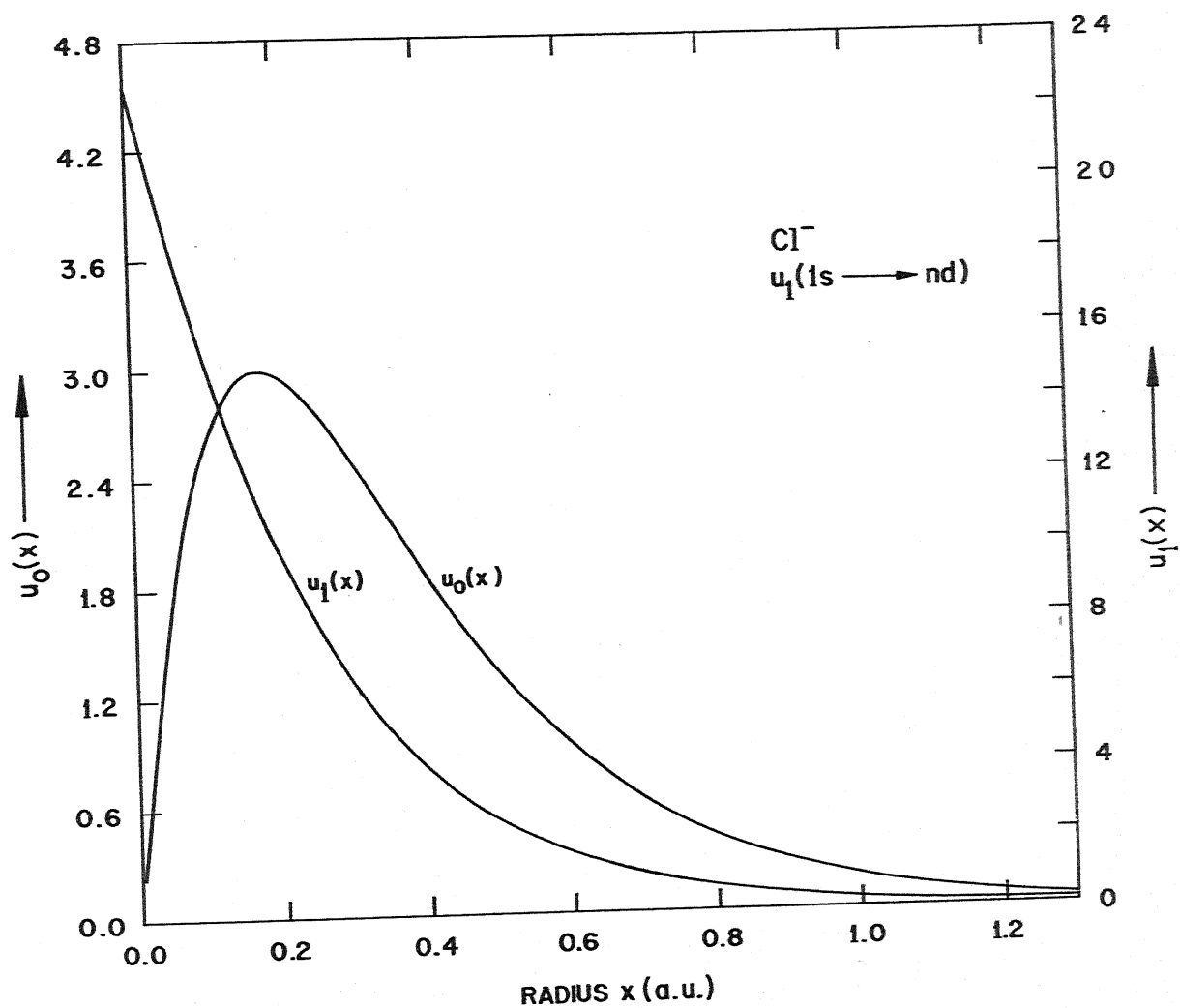
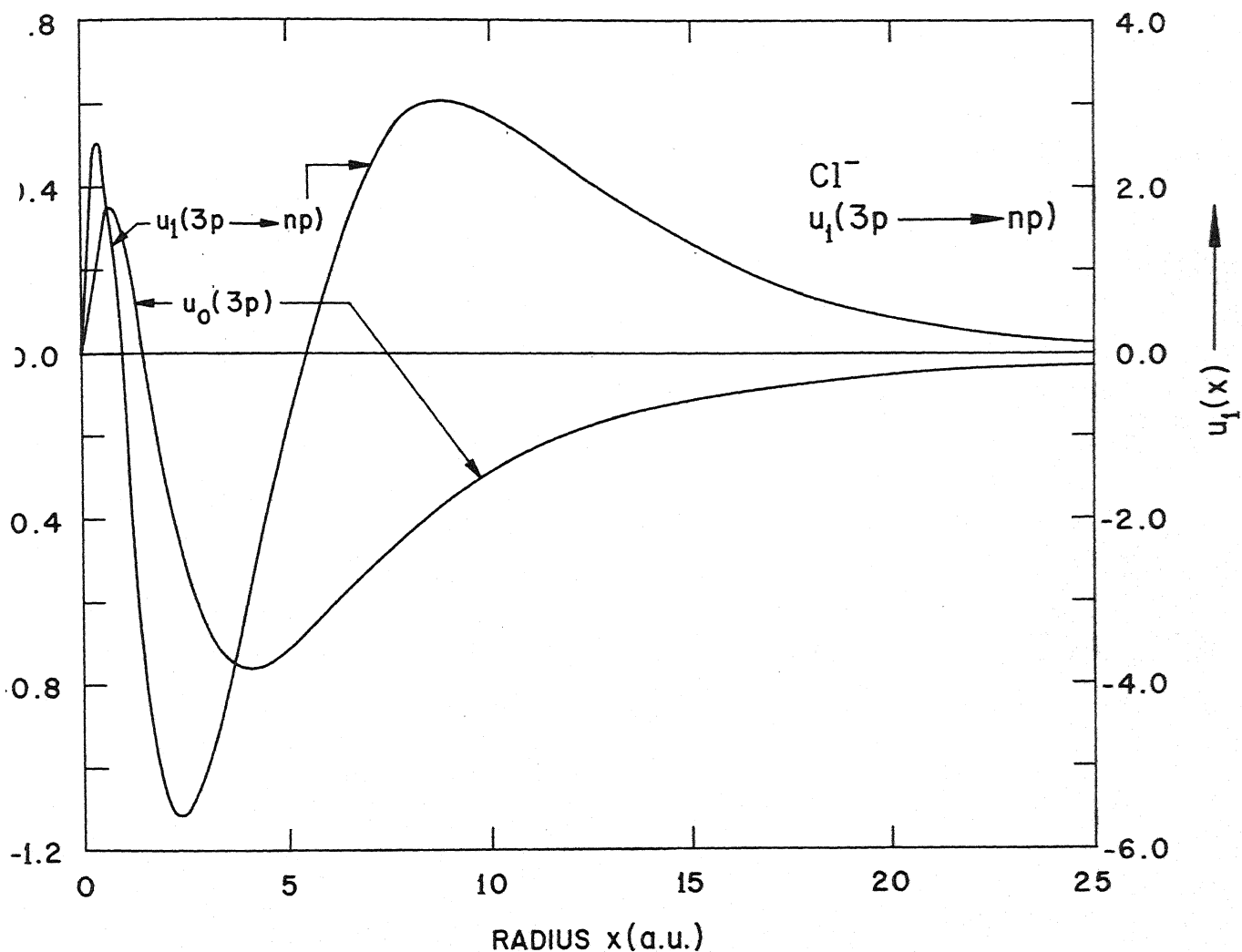


FIG. VI.2: THE 1s HFS FUNCTION $u_0(1s)$ AND ITS PERTURBATION $u_1(1s \rightarrow nd)$ FOR Cl^- . THE RIGHT-HAND ORDINATE SCALE PERTAINS TO u_1 ; THE LEFT-HAND ORDINATE SCALE PERTAINS TO u_0 .



VI.3: THE 3p HFS FUNCTION $u_0(3p)$ AND ITS PERTURBATION $u_1(3p \rightarrow np)$ FOR Cl^- . THE RIGHT-HAND ORDINATE SCALE PERTAINS TO u_1 ; THE LEFT-HAND ORDINATE SCALE PERTAINS TO u_0 .

TABLE VI.3

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Pr^{+++}

Distortion	Present Perturbation -Numerical Calculation	Other Calculations	
		Perturbation -Numerical	Perturbation -Variation
1	2	3	4
1s \rightarrow nd	0.0117	0.011 ^a	
2s \rightarrow nd	0.0257	0.027 ^a	
2p \rightarrow np	-0.2412	-0.240 ^a -0.243 ^b	-0.23 ^c
2p \rightarrow nf	0.0361	0.037 ^a	
3s \rightarrow nd	0.0512	0.046 ^a	
3p \rightarrow np	-1.4583	-1.507 ^a -1.545 ^b	-0.44 ^c
3p \rightarrow nf	0.0788	0.081 ^a	
3d \rightarrow ns	-0.0194	0.024 ^a	
3d \rightarrow nd	-0.3137	-0.325 ^a -0.322 ^b	-0.31 ^c
3d \rightarrow ng	0.0894	0.491 ^a	
4s \rightarrow nd	0.0971	0.086 ^a	
4p \rightarrow np	-7.9281	-8.842 ^a -8.81 ^b	-6.8 ^c
4p \rightarrow nf	0.1703	0.176 ^a	
4d \rightarrow ns	-0.0183	0.365 ^a	

Table VI.3 (Continued)

1	2	3	4
4d→nd	-2.4975	-2.878 ^a -2.83 ^b	-1.64 ^c
4d→ng	0.2261	0.239 ^a	
5s→nd	0.1500	0.238 ^a	
5p→np	-52.5955	-68.853 ^a -69.7 ^b	-98.1 ^c
4f→nf	-0.5536		
Total Angular	1.3853	2.158 ^a 2.5 ^b	2.54 ^c
Total Radial	-65.5879	-82.645 ^a	
Total	-64.2026	-80.487 ^a -80.9 ^b	-105.0 ^c

- a) Calculated by Ghatikar et al. (ref. 9) using Hartree functions of Ridley (ref. 54)
- b) Calculated by Sternheimer (ref. 6 and ref. 7) using Hartree functions of Ridley (ref. 54). The total angular contribution was, however, estimated using Thomas-Fermi model.
- c) Calculated by Wickner and Burns (ref. 15) using Hartree functions of Ridley (ref. 54).

TABLE VI.4

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Tm^{+++}

Distortion	Present Perturbation -Numerical Calculation	Other Calculations	
		Perturbation -Numerical	Perturbation -Variation
1	2	3	4
1s \rightarrow nd	0.0101	0.010 ^a	
2s \rightarrow nd	0.0217	0.022 ^a	
2p \rightarrow np	-0.1980	-0.196 ^a -0.196 ^b	-0.18 ^c
2p \rightarrow nf	0.0307	0.032 ^a	
3s \rightarrow nd	0.0459	0.040 ^a	
3p \rightarrow np	-1.1300	-1.240 ^a -1.175 ^b	-0.31 ^c
3p \rightarrow nf	0.0636	0.066 ^a	
3d \rightarrow ns	-0.0151	-0.003 ^a	
3d \rightarrow nd	-0.2346	-0.240 ^a -0.237 ^b	-0.23 ^c
3d \rightarrow ng	0.0722	0.074 ^a	
4s \rightarrow nd	0.0725	0.074 ^a	
4p \rightarrow np	-6.3191	-6.972 ^a -6.79 ^b	-6.5 ^c
4p \rightarrow nf	0.1402	0.138 ^a	
4d \rightarrow ns	-0.0179	0.136 ^a	

Table VI.4 (Continued)

1	2	3	4
4d→nd	-1.9498	-2.163 ^a -2.18 ^b	-1.20 ^c
4d→ng	0.1800	0.185 ^a	
5s→nd	0.2483	0.219 ^a	
5p→np	-49.8435	-64.773 ^a -67.2 ^b	-59.0 ^c
5p→nf	0.3323	0.392 ^a	
4f→nf	-2.9813		
Total Angular	1.1844	1.385 ^a 2.5 ^b	2.92 ^c
Total Radial	-62.6564	-75.584 ^a	
Total	-61.4720	-74.199 ^a -75.3 ^b	-61.5 ^c

- a) Calculated by Ghatikar et al. (ref. 9) using Hartree functions of Ridley (ref. 54).
- b) Calculated by Sternheimer (ref. 6 and ref. 7) using Hartree functions of Ridley (ref. 54). Total Angular contribution was, however, estimated using Thomas-Fermi model.
- c) Calculated by Wickner and Burns (ref. 15) using Hartree functions of Ridley (ref. 54).

TABLE VI.5

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Ce^{+++}

Distortion	Present Perturbation-Numerical Calculation	Watson-Freeman Calculation ^a
1	2	3
1s \rightarrow nd	0.0118	
2s \rightarrow nd	0.0267	
2p \rightarrow np	-0.2464	-1.5
2p \rightarrow nf	0.0370	
3s \rightarrow nd	0.0551	
3p \rightarrow np	-1.5035	-4.0
3p \rightarrow nf	0.0806	
3d \rightarrow ns	-0.0199	
3d \rightarrow nd	-0.3249	-0.50
3d \rightarrow ng	0.0912	
4s \rightarrow nd	0.1151	
4p \rightarrow np	-8.1778	-11.0
4p \rightarrow nf	0.1744	
4d \rightarrow ns	-0.0188	
4d \rightarrow nd	-2.5812	-2.50
4d \rightarrow ng	0.2326	
5s \rightarrow nd	0.2433	
5p \rightarrow np	-53.1045	-54.0
5p \rightarrow nf	0.4391	

Table VI.5 (Continued)

1	2	3
4f→nf	-0.2851	
Total Angular	1.4682	
Total Radial	-66.2236	-73.5
Total	-64.7554	

- a) Calculated by Freeman and Watson (ref. 23) using Self-Consistent-Field m_1 unrestricted Hartree-Fock method for complete solution.

SCF method and includes the distortion of the inner shells due to the large perturbation of the outer shells (for example the 5p-shell) also (apart from the distortion due to the crystal field). This is why the agreement for the values of γ_{∞} for the inner orbitals is not as good as that for the outer orbitals. However, the interesting agreement between $\gamma_{\infty}(nl - l')$ values calculated presently and those calculated by these authors for the outer orbitals show that HFS wave functions are reasonably good approximation to HF wave functions.

From Table VI.6 (which collects the $\gamma_{\infty}(nl - l')$ and γ_{∞} (total) values for Na^+ ion) also it is seen that HFS wave functions can be used to produce the γ_{∞} values to a fairly high degree of accuracy in the perturbation-numerical approach. From this table we see that $|\gamma_{\infty}|_{\text{HFS}}$ is slightly higher than $|\gamma_{\infty}|_{\text{HF}}$ and it is because of the fact that in the HFS scheme the outer orbitals do not seem to be as much contracted as in the HF scheme. It is encouraging to note that the γ_{∞} (total) for Na^+ obtained by us using HFS wave functions compare most favourably with the value obtained by Lahiri and Mukherji³¹ following their self-consistent perturbation procedure which is accurate in the coupled HF scheme. The unperturbed $u_0(2p)_{\text{HFS}}$ function and its perturbation $u_1(2p \rightarrow nf)_{\text{HFS}}$ for Na^+ are shown in Figure VI.4.

Table VI.7 contains the results of $\gamma_{\infty}(nl - l')$ for the In^{+++} ion. It also includes the results obtained by Sternheimer⁸ using the same procedure as the present one, but making use of the neutral atom HFS wave functions instead of the actual ion wave functions. Since the ionic wave functions are more internal we find that $|\gamma_{\infty}|$ calculated presently using HFS wave functions for the In^{+++} ion is less than that calculated using the HFS wave functions for the neutral In atom. The value obtained by Burns and Wickner¹⁴ using Hartree functions of Ridley⁵⁵ and the perturbation-variation method is -15.33. This is, however, very surprising because the use of Hartree wave functions is supposed to yield a $|\gamma_{\infty}|$ value higher

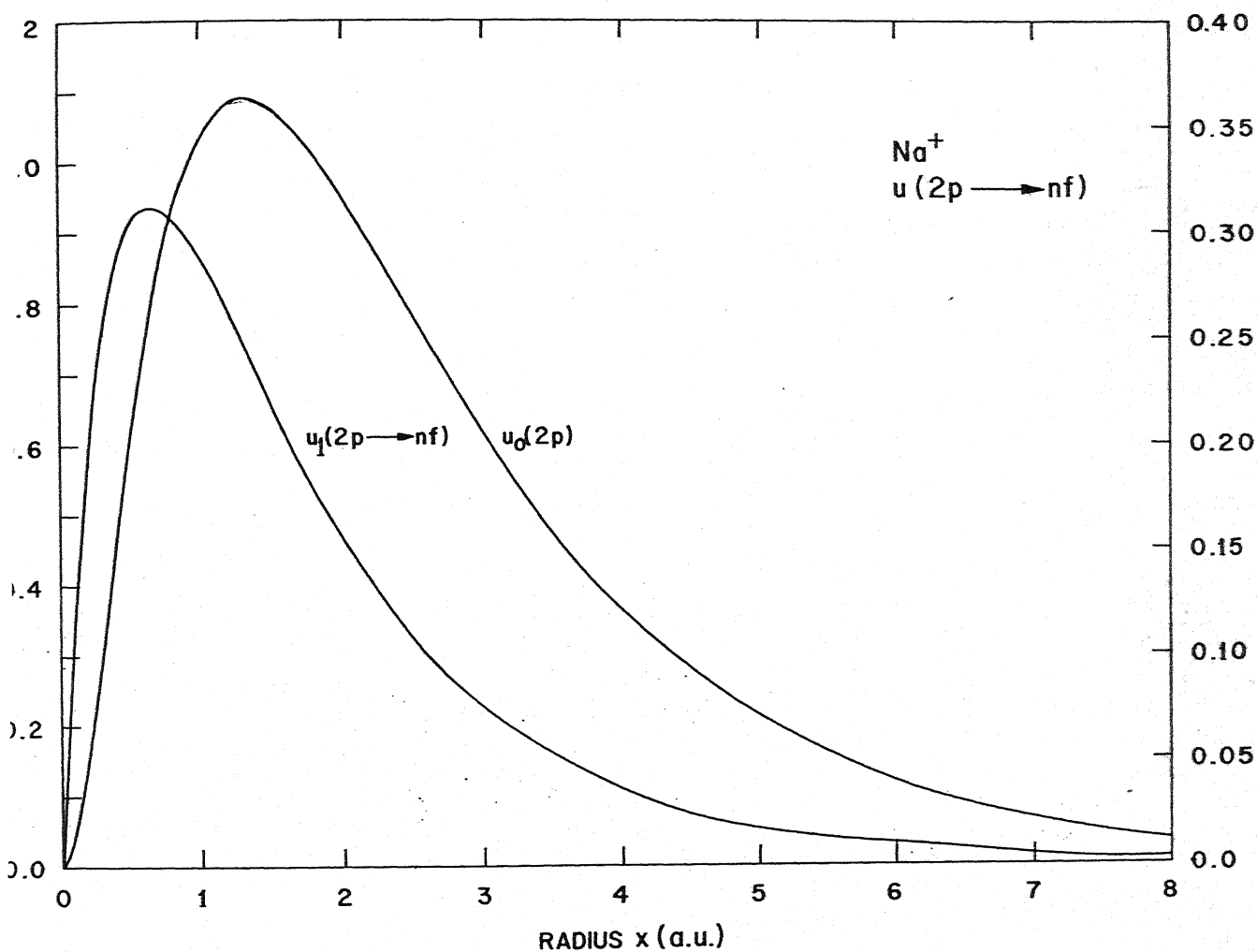


FIG. 4: THE 2p HFS FUNCTION $u_0(2p)$ AND ITS PERTURBATION $u_1(2p \rightarrow nf)$ FOR Na^+ . THE RIGHT-HAND ORDINATE SCALE PERTAINS TO u_1 ; THE LEFT-HAND ORDINATE SCALE PERTAINS TO u_0 .

TABLE VI.6

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Na^+

Distortion	Present Perturbation -Numerical Calculation	Other Calculations		
		Perturbation -Numerical	Perturbation -Variation	Other Methods
1	2	3	4	5
$1s \rightarrow nd$	0.0640	0.062 ^a	0.064 ^b	0.05872 ^c
$2s \rightarrow nd$	0.2279	0.234 ^a	0.326 ^b 0.3275 ^d	0.37200 ^c
$2p \rightarrow np$	-5.6274	-5.16 ^a -4.70 ^e	-5.23 ^b -5.28 ^d	
$2p \rightarrow nf$	0.3076	0.303 ^a	0.304 ^b 0.3065 ^d	-4.150 ^c ($2p \rightarrow np+nf$)
Total Angular	0.5995	0.599 ^a 0.6 ^e		
Total Radial	-5.6274	-5.16 ^a		
Total	-5.0279	-4.561 ^a -4.10 ^e	-4.534 ^b -4.6460 ^d	-4.497 ^c -5.178 ^f

a) Calculated by Sternheimer (ref. 6). For 2s and 2p orbitals Hartree-Fock functions of Hartree and Hartree (ref. 59) and Löwdin's (ref. 53) analytic fit to the Hartree-Fock function of Hartree and Hartree (ref. 59) were used. The $1s \rightarrow nd$ contribution is approximated using hydrogenic wave function (ref. 2).

b) Calculated by Das and Bersohn (ref. 10) using Löwdin's (ref. 53) analytic fit to Hartree-Fock wave functions of Hartree and Hartree (ref. 59).

-Contd.

Table VI.6 (Continued)

- c) Calculated by Langhoff and Hurst (ref. 29) within the framework of an uncoupled HF scheme, subject to proviso that the exchange part of the Fock potential be expressible as a multiplicative function. These authors used analytic Hartree-Fock function of Bagus (ref. 60). They also report values of -4.514 and -4.505 for total antishielding factor using analytic Hartree-Fock functions of Clementi (ref. 61) and Sachs (ref. 62).
- d) Calculated by Burns (ref. 13) using the Hartree-Fock wave functions of Hartree and Hartree (ref. 59).
- e) Calculated by Sternheimer and Foley (ref. 5) using Hartree-Fock wave function of Fock and Petrashen (ref. 63) for 3p orbital. Total angular contribution was, however, calculated by Foley and coworkers (ref. 3) using the above Hartree-Fock wave functions.
- f) Calculated by Lahiri and Mukherji (ref. 31) following their self-consistent perturbation procedure (ref. 30). The result is accurate in coupled HF scheme.

TABLE VI.7

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for In^{+++}

Distortion	Present Perturbation -Numerical Calculation	Other Calculations	
		Perturbation -Numerical	Perturbation -Variation
1	2	3	4
		(a)	(b)
1s \rightarrow nd	0.0141		
2s \rightarrow nd	0.0325		
2p \rightarrow np	-0.3082	-0.31	-0.32
2p \rightarrow np	0.0445		
3s \rightarrow nd	0.0656		
3p \rightarrow np	-2.0770	-2.13	-1.06
3p \rightarrow nf	0.1022		
3d \rightarrow ns	-0.0266		
3d \rightarrow nd	-0.4791	-0.51	-0.55
3d \rightarrow ng	0.1158		
4s \rightarrow nd	0.1579		
4p \rightarrow np	-14.7440	-15.77	-7.41
4p \rightarrow nf	0.2543		
4d \rightarrow ns	-0.0143		
4d \rightarrow nd	-7.1171	-8.40	-7.89
4d \rightarrow ng	0.3707		

Table VI.7 (Continued)

1	2	3	4
		(a)	(b)
Total Angular	1.1177	2.2	1.9
Total Radial	-24.7254		
Total	-23.6077	-24.9	-15.33

- a) Calculated by Sternheimer (to be published, Private Communication) using Hartree-Fock-Slater wave functions (ref. 32) for neutral In atom. He, however estimated that the values calculated thus, using neutral atom wave functions instead of actual ionic wave functions will overestimate the result by about $\leq 5\%$. The ionic wave functions are more internal and therefore the absolute value of the antishielding factor decreases when actual ionic wave functions are used. The total angular contribution was estimated using Thomas-Fermi model. Only $4p \rightarrow np$ and $4d \rightarrow nd$ contributions were actually calculated. The rest of them were found by interpolation or extrapolation.
- b) Calculated by Burns and Wickner (ref. 14) using Hartree wave functions of Ridley (ref. 55).

than that obtained using the HF or HFS wave functions. Presumably, this unexpected result is due to some error in the calculations of Burns and Wickner.

Table VI.8 contains the values of γ_{∞} ($nl \rightarrow l'$) and total γ_{∞} for the ions Y^{+++} , Bi^{+++} and Am^{++} calculated presently with HFS wave functions for these ions and also the corresponding values calculated by Sternheimer⁸ using the neutral atom HFS wave functions for the respective ions. The perturbation $u_1(3d \rightarrow ng)_{\text{HFS}}$ and the unperturbed $u_0(3d)_{\text{HFS}}$ functions for Y^{+++} are shown in Figure VI.5.

Table VI.9 contains the results of R factor calculations in the perturbation-numerical formalism for the rare earth ions Pr^{+++} , Tm^{+++} and Ce^{+++} pertaining to the 4f-valence electron. As has been said earlier the values of R factor calculated in the present investigation are not as reliable as those for γ_{∞} factor. The present values, however, may be taken as rough estimates utilizing the HFS wave functions. For Pr^{+++} and Tm^{+++} ions we can compare our results with the corresponding results of Sternheimer⁷ and Ghatikar et al.⁹ both of which utilize Hartree wave functions of Ridley⁵⁴. Sternheimer, however, uses the HF functions of Freeman and Watson⁵⁶ for the 4f valence electrons in these ions. We shall, compare our results with those of Ghatikar et al. only. It is found by this comparison that the use of the HFS wave functions instead of H wave functions brings down the value of R(total). It would be, however, interesting to compare our R_{HFS} values with R_{HF} values for these systems. Unfortunately the HF wave functions and hence R_{HF} values are not available. The refinements in the procedure for calculating u_1 , the perturbation in the

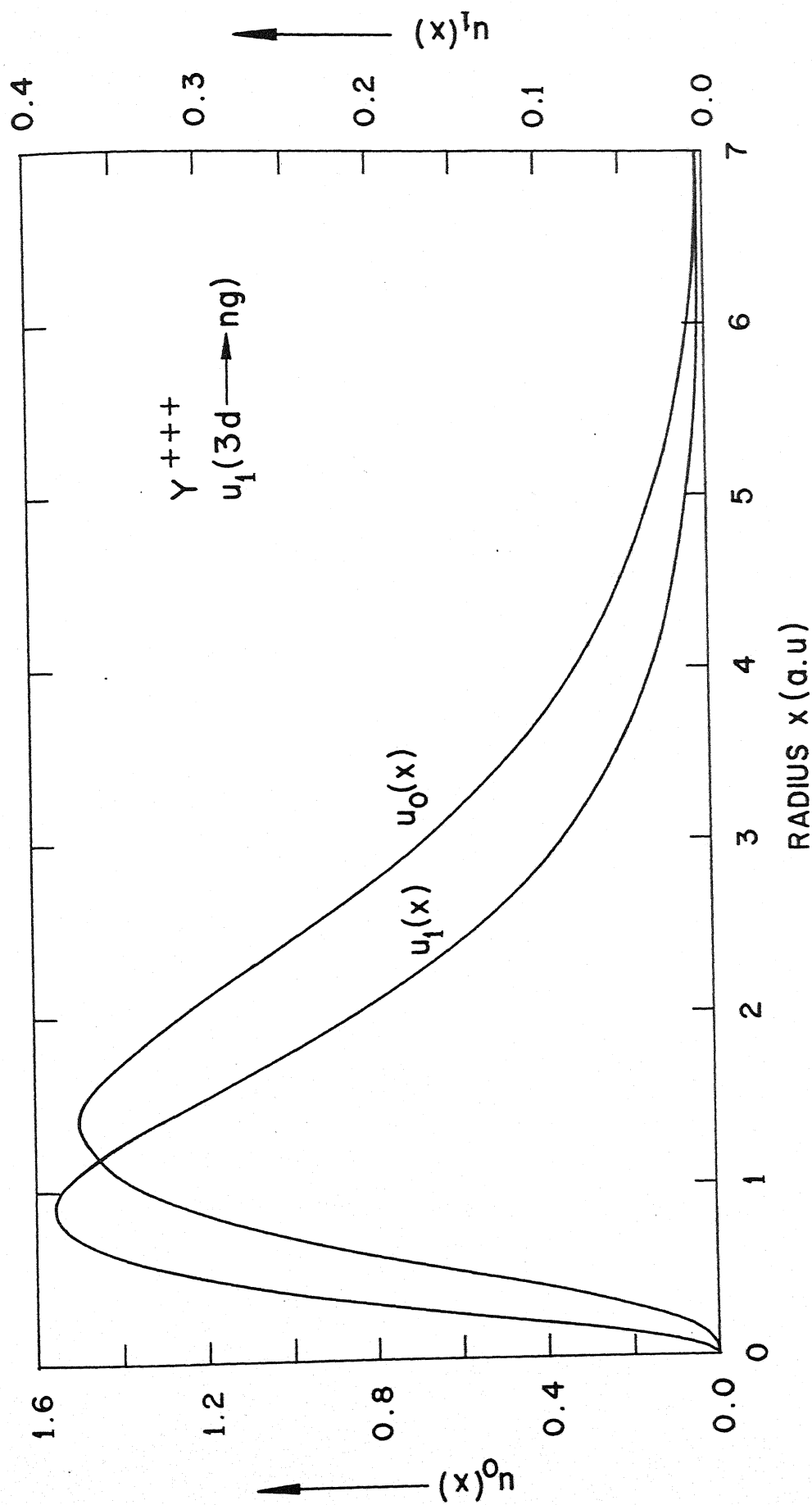


FIG. VI.5: THE 3d HFS FUNCTION $u_0(3d)$ AND ITS PERTURBATION $u_1(3d \rightarrow ng)$ FOR Y^{+++} . THE RIGHT-HAND ORDINATE SCALE PERTAINS TO u_1 ; THE LEFT-HAND ORDINATE SCALE PERTAINS TO u_0 .

TABLE VI.8

Values of $\gamma_{\infty}(nl \rightarrow l')$ and Total γ_{∞} for Y^{+++} , Bi^{+++} and Am^{++} Ions*

Distortion	Ion		
	Y^{+++}	Bi^{+++}	Am^{++}
1	2	3	4
$1s \rightarrow nd$	0.0176 ^a	0.0083 ^a	0.0072 ^a
$2s \rightarrow nd$	0.0415 ^a	0.0178 ^a	0.0154 ^a
$2p \rightarrow np$	-0.4077 ^a	-0.1585 ^a	-0.1352 ^a
	-0.42 ^b	-0.16 ^b	-0.13 ^b
$2p \rightarrow nf$	0.0572 ^a	0.0252 ^a	0.0222 ^a
$3s \rightarrow nd$	0.0951 ^a	0.0354 ^a	-0.0354 ^a
$3p \rightarrow np$	-3.4463 ^a	-0.8584 ^a	-0.7077 ^a
	-3.49 ^b	-0.87 ^b	-0.69 ^b
$3p \rightarrow nf$	0.1449 ^a	0.0501 ^a	0.0423 ^a
$3d \rightarrow ns$	-0.0399 ^a	-0.0116 ^a	-0.0096 ^a
$3d \rightarrow nd$	-0.9595 ^a	-0.1732 ^a	-0.1406 ^a
	-0.98 ^b	-0.17 ^b	-0.14 ^b
$3d \rightarrow ng$	0.1701 ^a	0.0570 ^a	0.0481 ^a
$4s \rightarrow nd$	0.2882 ^a	0.0621 ^a	0.0455 ^a
$4p \rightarrow np$	-27.1319 ^a	-4.1745 ^a	-3.0641 ^a
	-30.88 ^b	-4.30 ^b	-3.1 ^b
$4p \rightarrow nf$	0.4122 ^a	0.1065 ^a	0.0840 ^a
$4d \rightarrow ns$		-0.0141 ^a	-0.0091 ^a
$4d \rightarrow nd$		-1.1284 ^a	-0.7678 ^a
		-1.16 ^b	-0.70 ^b

Table VI.8 (Continued)

1	2	3	4
4d → ng		0.1309 ^a	0.1039 ^a
4f → nf		-0.7758 ^a	-0.4149 ^a
		-0.72 ^b	-0.40 ^b
5s → nd		0.1241 ^a	0.0972 ^a
5p → np		-24.3411 ^a	-14.1679 ^a
		-25.99 ^b	-15.21 ^b
5p → nf		0.2870 ^a	0.1787 ^a
5d → ns		0.0061 ^a	0.0111 ^a
		1.388 ^b	
5d → nd		-10.5391 ^a	-4.7389 ^a
		-12.05 ^b	-5.19 ^b
5d → ng		0.3693 ^a	0.2396 ^a
5f → nf			-5.0269 ^a
			-4.77 ^b
6s → nd		0.5310 ^a	0.2721 ^a
6p → np			-106.4563 ^a
			-110.50 ^b
6p → nf			0.0856 ^a
Total Angular	1.1868 ^a	1.7851 ^a	1.1987 ^a
	2.2 ^b	3.0 ^b	3.5 ^b
Total Radial	-31.9454 ^a	-42.1435 ^a	-135.6203 ^a
Total	-30.7586 ^a	-40.3584 ^a	-134.4216 ^a
	-33.6 ^b	-42.4 ^b	-137.3 ^b

-Contd.

Table VI.8 (Continued)

- *) For these ions no Hartree or Hartree-Fock values exists.
- a) Present perturbation-numerical calculations using Hartree-Fock-Slater wave functions (ref. 32) for the corresponding ions. As has been mentioned in the text the contributions from $nd \rightarrow ns$ type of excitations are not reliable because of the fact that the procedure employed in the present work is not well-suited for such a case where the solution is highly unstable.
- b) Calculations made by Sternheimer (to be published, Private Communication) using Perturbation-Numerical Procedure. He, however, uses the neutral atom HFS wave functions in place of the actual ionic wave functions. According to his estimate the overestimate of the absolute value of the antishielding factor due to the use of the neutral atom wave functions instead of the actual ionic wave functions is $\leq 5\%$. See also footnote 'a' of Table VI.4. Sternheimer actually calculates contributions from $3p \rightarrow np$ and $3d \rightarrow nd$ excitations for Y, contributions from $4p \rightarrow np$, $4d \rightarrow nd$, $4f \rightarrow nf$, $5p \rightarrow np$ and $5d \rightarrow nd$ excitations for Bi and contributions from $5p \rightarrow np$, $5d \rightarrow nd$, $5f \rightarrow nf$ and $6p \rightarrow np$ excitations for Am. Rest of the radial excitation contributions were extrapolated or interpolated. Contribution from only one angular excitation, namely $5d \rightarrow ns$ for Bi was actually calculated. The total angular contributions given here are obtained using Thomas-Fermi model.

TABLE VI.9

Values of $R(nl \rightarrow l')$ and Total R for Pr^{+++} , Tm^{+++} and Ce^{+++} Ions Pertaining to the 4f Valence Electron in them

Distortion	Ion		
	Pr^{+++}	Tm^{+++}	Ce^{+++}
1	2	3	4
$1s \rightarrow nd$	0.0117 ^a	0.0101 ^a	0.0118 ^a
	0.002 ^b	0.00 ^b	
$2s \rightarrow nd$	0.0247 ^a	0.0206 ^a	0.0257 ^a
	0.022 ^b	0.019 ^b	
$2p \rightarrow np$	-0.2228 ^a	-0.1796 ^a	-0.2283 ^a
	-0.171 ^b	-0.125 ^b	
$2p \rightarrow nf$	0.0352 ^a	0.0298 ^a	0.0361 ^a
	0.029 ^b	0.026 ^b	
$3s \rightarrow nd$	0.0331 ^a	0.0279 ^a	0.0361 ^a
	0.030 ^b	0.024 ^b	
$3p \rightarrow np$	-0.5825 ^a	-0.3910 ^a	-0.6132 ^a
	-0.657 ^b	-0.470 ^b	
$3p \rightarrow nf$	0.0537 ^a	0.0410 ^a	0.0553 ^a
	0.058 ^b	0.043 ^b	
$3d \rightarrow ns$	-0.0182 ^a	-0.0142 ^a	-0.0187 ^a
	0.008 ^b	-0.006 ^b	
$3d \rightarrow nd$	-0.1463 ^a	-0.1015 ^a	-0.1532 ^a
	-0.162 ^b	-0.107 ^b	

Table VI.9 (Continued)

1	2	3	4
3d → ng	0.0667 ^a 0.070 ^b	0.0522 ^a 0.053 ^b	0.0682 ^a
4s → nd	0.0177 ^a 0.018 ^b	0.0107 ^a 0.011 ^b	0.2221 ^a
4p → np	0.1927 ^a 0.071 ^b	0.1983 ^a 0.161 ^b	0.1828 ^a
4p → nf	0.0326 ^a 0.037 ^b	0.0229 ^a 0.023 ^b	0.0341 ^a
4d → ns	-0.0134 ^a 0.027 ^b	-0.0102 ^a 0.003 ^b	-0.0139 ^a
4d → nd	0.0648 ^a 0.046 ^b	0.0573 ^a 0.055 ^b	0.0648 ^a
4d → ng	0.0402 ^a 0.045 ^b	0.0287 ^a 0.033 ^b	0.0420 ^a
5s → nd	0.0025 ^a 0.005 ^b	0.0030 ^a 0.003 ^b	0.0045 ^a
5p → np	0.5133 ^a 0.710 ^b	0.3279 ^a 0.396 ^b	0.5448 ^a
5p → nf	0.0072 ^a 0.012 ^b	0.0041 ^a 0.006 ^b	0.0073 ^a
Total Angular	0.2937 ^a 0.363 ^b 0.2952 ^c	0.2266 ^a 0.240 ^b 0.2252 ^c	0.3108 ^a

Table VI.9 (Continued)

1	2	3	4
Total Radial	-0.1808 ^a	-0.0885 ^a	-0.2022 ^a
	-0.163 ^b	-0.090 ^b	
	-0.1644 ^c	-0.0951 ^c	
Total	0.1129 ^a	0.1381 ^a	0.1086 ^a
	0.200 ^b	0.150 ^b	
	0.1308 ^c	0.1296 ^c	

- a) Present Perturbation-Numerical Calculations using Hartree-Fock-Slater wave functions (ref. 32). As has been mentioned in the text the contributions from the angular excitations are not quite reliable. Since here the contributions of angular excitations are as important as those of radial excitations, the total R values are also not quite reliable.
- b) Calculated by Ghatikar and coworkers (ref. 9) using Perturbation-Numerical approach and Hartree wave functions of Ridley (ref. 54).
- c) Calculated by Sternheimer (ref. 7) using Perturbation-Numerical approach and Hartree functions of Ridley (ref. 54). He, however, uses HF function of Freeman and Watson (ref. 56) for 4f-orbital. The angular contribution is calculated using Thomas-Fermi model.

wave functions, especially for the angular excitations may lead to a more complete evaluation of the HFS wave functions. Further work along these lines is in progress.

VI.7 CONCLUSION

From the discussion of the previous section it is clear that the use of HFS wave functions in the perturbation-numerical approach of Sternheimer reproduces the values of γ_{∞} factors for positive ions sufficiently close to the values obtained by the use of HF wave functions. Inclusion of exchange in the HF formalism contracts the outer orbital wave functions and this results in the fact that $|\gamma_{\infty}|$ value obtained using Hartree wave functions is higher than that obtained using HF wave functions in the perturbation-numerical or perturbation-variation approach. The fact that $|\gamma_{\infty}|$ values obtained presently using HFS wave functions are slightly higher than those obtained using HF wave functions indicates that the Slater free-electron exchange approximation and its tail correction as carried out by Herman and Skillman are slightly less effective than the actual exchange terms of the Hartree-Fock equations in contracting the outer orbitals of the atomic systems. On the other hand, in the previous Chapters we have concluded that Slater free-electron exchange approximation with the tail correction overemphasizes the role of exchange. Hence we conclude here that this overemphasis is not due to the overcontraction of the outer orbitals. This statement is also supported by the fact that the HFS results of diamagnetic susceptibilities are in good agreement with the corresponding HF results whereas the agreement between HFS nuclear magnetic shielding values with the

corresponding HF values was not as good. The present investigation suggests that a modification of the Slater free-electron exchange potential in the inner regions as well might improve the HFS wave functions. Efforts in this direction will be rewarding.

REFERENCES

1. R.M. Sternheimer, Phys. Rev., 80, 102 (1950); 84, 244 (1951); 86, 316 (1952).
2. R.M. Sternheimer and H.M. Foley, Phys. Rev., 92, 1460 (1953).
3. H.M. Foley, R.M. Sternheimer and D. Tyko, Phys. Rev., 93, 734 (1954).
4. R.M. Sternheimer, Phys. Rev., 95, 736 (1954); 96, 951 (1954).
5. R.M. Sternheimer and H.M. Foley, Phys. Rev., 102, 731 (1956).
6. R.M. Sternheimer, Phys. Rev., 107, 1565 (1957); 115, 1198 (1959); 123, 870 (1961); 127, 812 (1962); 130, 1423 (1963); 132, 1637 (1963).
7. R.M. Sternheimer, Phys. Rev., 146, 140 (1966).
8. R.M. Sternheimer, to be published (private communication).
9. M.N. Ghatikar, A.K. Raychaudhari and D.K. Ray, Proc. Phys. Soc. (London), 86, 1239 (1965).
10. T.P. Das and R. Bersohn, Phys. Rev., 100, 1792(A) (1958); 102, 733 (1956).
11. E.G. Wikner and T.P. Das, Phys. Rev., 107, 497 (1957); 109, 360 (1958).
12. G. Burns, Phys. Rev., 115, 357 (1959).
13. G. Burns, J. Chem. Phys., 31, 1253 (1959).
14. G. Burns and E.G. Wikner, Phys. Rev., 121, 155 (1961).
15. E.G. Wikner and G. Burns, Phys. Letters, 2, 225 (1962).
16. R. Ingalls, Phys. Rev., 128, 1155 (1962).
17. A. Dalgarno, Proc. Roy. Soc. (London), A251, 282 (1959).
18. A. Dalgarno, in "Advances in Physics", Ed. N.F. Mott, Taylor and Francis Ltd., London (1962), Vol. 11, page 281.
19. S. Kaneko, J. Phys. Soc. (Japan), 14, 1600 (1959).
20. L.C. Allen, Phys. Rev., 118, 167 (1960).
21. P.G. Khubchandani, R.R. Sharma and T.P. Das, Phys. Rev., 126, 594 (1962).

22. R.E. Watson and A.J. Freeman, Phys. Rev., 123, 521 (1961); 131, 250, 2566 (1963).
23. A.J. Freeman and R.E. Watson, Phys. Rev., 132, 706 (1963).
24. R.E. Watson and A.J. Freeman, Phys. Rev., 135, A1209 (1964).
25. H.D. Cohen, J. Chem. Phys., 43, 3558 (1965).
26. H.D. Cohen, J. Chem. Phys., 45, 10 (1966).
27. H.D. Cohen and C.C.J. Roothaan, J. Chem. Phys., 43, S34 (1965).
28. M. Yoshimine and R.P. Hurst, Phys. Rev., 135, A612 (1964).
29. P.W. Langhoff and R.P. Hurst, Phys. Rev., 139, A1415 (1965).
30. J. Lahiri and A. Mukherji, J. Phys. Soc. (Japan), 21, 1178 (1966).
31. J. Lahiri and A. Mukherji, Phys. Rev., 141, 428 (1966); 153, 386 (1967); 155, 24 (1967).
32. F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice-Hall Inc., Englewood Cliffs, New Jersey (1963).
33. See for example, ref. 7, ref. 12, ref. 13, ref. 28 and ref. 29.
34. E.G. Wikner, W.E. Blumberg and E.L. Hahn, Phys. Rev., 118, 631 (1960).
35. H. Kawamura, E. Otsuka and K. Ishiwatari, J. Phys. Soc. (Japan), 11, 1064 (1956).
36. E. Otsuka and H. Kawamura, J. Phys. Soc. (Japan), 12, 1071 (1957).
37. E. Otsuka, J. Phys. Soc. (Japan), 13, 1155 (1958).
38. W.G. Proctor and W. Tanttilla, Phys. Rev., 98, 1854 (1955); 101, 1757 (1956).
39. W.G. Proctor and W.A. Robinson, Phys. Rev., 104, 1344 (1956).
40. D.A. Jennings, W.H. Tanttilla and O. Kraus, Phys. Rev., 109, 1059 (1958).
41. E.F. Taylor and N. Bloembergen, Phys. Rev., 113, 431 (1959).
42. D.I. Bolef and M. Menes, Phys. Rev., 114, 1441 (1959).
43. R.L. Mössbauer, Rev. Mod. Phys., 36, 362 (1964).
44. R.G. Barnes, R.L. Mössbauer, E. Kankaleit and J.M. Poindexter, Phys. Rev., 136, A175 (1964).

45. D.R. Hartree, "Atomic Structure Calculations", John Wiley & Sons, Inc., New York (1957), Chapter 4.
46. L.M. Milne-Thomson, "Calculus of Finite Differences", Macmillan (1933).
47. F.B. Hildebrand, "Introduction to Numerical Analysis", McGraw Hill Book Co. (1956).
48. R.M. Sternheimer, Private Communication.
49. D.R. Hartree, Proc. Roy. Soc. (London), A151, 96 (1935).
50. D.R. Hartree, Proc. Roy. Soc. (London), A141, 282 (1933).
51. C. Froese, Proc. Cambridge Phil. Soc., 53, 206 (1957).
52. D.R. Hartree and W. Hartree, Proc. Roy. Soc. (London), A156, 45 (1936).
53. P.O. Löwdin, Phys. Rev., 90, 120 (1953).
54. E.C. Ridley, Proc. Cambridge Phil. Soc. (London), 56, 41 (1960).
55. E.C. Ridley, Proc. Cambridge Phil. Soc. (London), 52, 698 (1956).
56. A.J. Freeman and R.E. Watson, Phys. Rev., 127, 2058 (1962).
57. E. Clementi, J. Chem. Phys., 38, 996 (1963).
58. E. Clementi, A.D. McLean, D.L. Raimondi and M. Yoshimine, Phys. Rev., 133, A1274 (1964).
59. D.R. Hartree and W. Hartree, Proc. Roy. Soc. (London), A193, 299 (1948).
60. F. Bagus, Phys. Rev., 139, A619 (1965).
61. See ref. 57
62. L.M. Sachs, Phys. Rev., 124, 1283 (1961).
63. V. Fock and M. Petrashen, Phys. Z. Sowjetunion, 6, 368 (1934).

45. D.R. Hartree, "Atomic Structure Calculations", John Wiley & Sons, Inc., New York (1957), Chapter 4.
46. L.M. Milne-Thomson, "Calculus of Finite Differences", Macmillan (1933).
47. F.B. Hildebrand, "Introduction to Numerical Analysis", McGraw Hill Book Co. (1956).
48. R.M. Sternheimer, Private Communication.
49. D.R. Hartree, Proc. Roy. Soc. (London), A151, 96 (1935).
50. D.R. Hartree, Proc. Roy. Soc. (London), A141, 282 (1933).
51. C. Froese, Proc. Cambridge Phil. Soc., 53, 206 (1957).
52. D.R. Hartree and W. Hartree, Proc. Roy. Soc. (London), A156, 45 (1936).
53. P.O. Löwdin, Phys. Rev., 90, 120 (1953).
54. E.C. Ridley, Proc. Cambridge Phil. Soc. (London), 56, 41 (1960).
55. E.C. Ridley, Proc. Cambridge Phil. Soc. (London), 52, 698 (1956).
56. A.J. Freeman and R.E. Watson, Phys. Rev., 127, 2058 (1962).
57. E. Clementi, J. Chem. Phys., 38, 996 (1963).
58. E. Clementi, A.D. McLean, D.L. Raimondi and M. Yoshimine, Phys. Rev., 133, A1274 (1964).
59. D.R. Hartree and W. Hartree, Proc. Roy. Soc. (London), A193, 299 (1948).
60. F. Bagus, Phys. Rev., 139, A619 (1965).
61. See ref. 57
62. L.M. Sachs, Phys. Rev., 124, 1283 (1961).
63. V. Fock and M. Petrashen, Phys. Z. Sowjetunion, 6, 368 (1934).

APPENDIX A

APPENDIX A

Here we make use of the relation (See eqn. 3.19, Chapter III)

$$\sigma_n(Z) = - \frac{\alpha^2}{3} \frac{\partial E_n(Z)}{\partial Z} \quad (\text{A.1})$$

to evaluate the nuclear magnetic shielding (σ_{HF}) values for the various isoelectronic series ($n = 2$ to $n = 27$) for which HF total energy values are available from the work of Clementi (See ref. 3, Chapter III) on the analytic HF wave functions of the positive ion isoelectronic series ($n = 2$ to $n = 27$). We have fitted the energy values by least square method to a three-term polynomial of the type

$$E_n(Z) = A_n Z^2 + B_n Z + C_n \quad (\text{A.2})$$

since this was found in general to be the best one for all the isoelectronic series considered. Indeed, a simple power series type of expansion in Z with four terms was tried and found to yield poorer results for many isoelectronic series. Details of the least square method of polynomial fitting are well known (See refs. 22 and 23, Chapter III). Table A.1 gives the results of the least square fitting. The calculated energy values using the polynomials obtained and the standard error data are also given there.

From equations (A.1) and (A.2) we get

$$\sigma_n(Z) = - \frac{\alpha^2}{3} (A_n Z + B_n) \quad (\text{A.3})$$

which is the equation used for evaluating the nuclear magnetic shielding

values for the various members of the isoelectronic series containing n electrons. Using the relationship (A.3) and the coefficients A_n and B_n appearing in the polynomial $E_n(Z)$ collected in Table A.1 we calculated the nuclear magnetic shielding values for the neutral atoms ($Z=n$) and singly, doubly and triply charged positive ($Z = n+1, n+2$ and $n+3$) and negative ($Z = n-1, n-2$ and $n-3$) ions for the various isoelectronic series containing two ($n=2$) to twentyseven ($n=27$) electrons. The σ_{HF} values obtained thus for the neutral atoms and singly charged positive and negative ions are given in Table A.2. This table also contains, for comparison, the corresponding σ_{HF} values calculated by Malli and Fraga (see ref. 18, Chapter III) using directly analytic HF wave functions. As can be seen here, the values of the present calculations agree very well with those of Malli and Fraga showing thereby that the present method is almost as powerful as the direct quantum mechanical calculation using the wave functions. This is, of course, a consequence of the fact that the SCF wave functions are stable (see ref. 2, Chapter III) under one-electron perturbation such as the one considered here, namely a change in the atomic number Z .

It should be noted here that from $n = 2$ to $n = 18$ the isoelectronic series used for getting the polynomials $E_n(Z)$ were of the type $A(Z)$, $B^+(Z+1)$, $C^{++}(Z+2)$, $D^{+++}(Z+3)$, $E^{++++}(Z+4)$; for $n = 19$ it was Sc^{++} , Ti^{+++} , V^{++++} , Cr^{+++++} , Mn^{+++++} and from $n = 20$ to $n = 27$ these were of the type $A^+(Z')$, $B^{++}(Z'+1)$, $C^{+++}(Z'+2)$, $D^{++++}(Z'+3)$, $E^{+++++}(Z'+4)$. Although we did not use the energy data on negative ions in the process of getting the polynomials $E_n(Z)$, we see that the shielding

values obtained for the negative ions are as good as those for the neutral atoms and the positive ions. Furthermore, for $n = 19$ the agreement between our shielding values and those of Malli and Fraga is also encouraging especially in view of the fact that the neutral atom and singly charged positive ion energy data were not available to us. From $n = 20$ to $n = 27$ the agreement between our shielding values and those directly calculated using wave functions for the neutral atoms is also worth noticing.

Table A.3 contains the σ_{HF} values obtained by the present procedure for doubly and triply charged positive and negative ions of the various isoelectronic series. These values are considered reliable in view of the discussion given above. It is interesting to note that we have here made available σ_{HF} values for doubly and triply charged negative ions for which HF wave functions are not available!

In conclusion we wish to point out that the present procedure for evaluating the shielding values seems to be a very useful one. It, however, requires the knowledge of the SCF total energy values for four or five members of each isoelectronic series.

TABLE A.1

HF Energy Polynomial and Standard Error Data

Isoelec. Series No.	No. of Electrons (n)	State	Atom/Ions in the Series	Total HF Energy* $-E_1(Z)$ (Rydbergs)	Fitted Energy $-E_n(Z)$ (Rydbergs)	Polynomial Fitted	
						$E_n(Z) = A_n Z^2 + B_n Z + C_n$	
1	2	3	4	5	6	7	
1	2	Ground	He	2.8617	2.8617	$E_2(Z) = -1.0000Z^2 + .62544Z - .11240$	
			Li ⁺	7.2364	7.2364		
			Be ⁺⁺	13.611	13.611		
			B ⁺⁺⁺	21.986	21.986		
			C ⁺⁺⁺⁺	32.361	32.361		
				7.4327	7.4324		
2	3	"	Li	14.277	14.278	$E_3(Z) = -1.1260Z^2 + 1.0362Z - .40716$	
			Be ⁺	23.576	23.576		
			B ⁺⁺	34.726	34.725		
			C ⁺⁺⁺	48.327	48.327		
			N ⁺⁺⁺⁺				

Table A.1 (Continued)

1	2	3	4	5	6	7	8
3	4	Ground	Be	14.573	14.573	$E_4(Z) = -1.2518Z^2 + 1.5997Z - .94316$	0.11×10^{-2}
			B ⁺	24.238	24.239		
			C ⁺⁺	36.408	36.408		
			N ⁺⁺⁺	51.082	51.081		
			O ⁺⁺⁺⁺	68.258	68.258		
4	5	"	B	24.529	24.528	$E_5(Z) = -1.3780Z^2 + 2.3929Z - 2.0415$	0.16×10^{-2}
			C ⁺	37.292	37.294		
			N ⁺⁺	52.816	52.816		
			O ⁺⁺⁺	71.095	71.093		
			F ⁺⁺⁺⁺	92.127	92.127		
5	6	"	C	37.689	37.688	$E_6(Z) = -1.5040Z^2 + 3.3498Z - 3.6426$	0.19×10^{-2}
			N ⁺	53.888	53.890		
			O ⁺⁺	73.100	73.100		
			F ⁺⁺⁺	95.320	95.318		
			Ne ⁺⁺⁺⁺	120.54	120.54		

Table A.1 (Continued)

1	2	3	4	5	6	7
6	6	$1D$	C	37.631	37.630	$E_6(Z) = -1.5043Z^2 + 3.3774Z - 3.7389$
			N^+	53.807	53.809	
			O^{++}	72.997	72.997	
			F^{+++}	95.195	95.193	
			Ne^{++++}	120.40	120.40	
7	6	$1S$	C	37.549	37.548	$E_6(Z) = -1.5047Z^2 + 3.4174Z - 3.8825$
			N^+	53.690	53.692	
			O^{++}	72.846	72.846	
			F^{+++}	95.011	95.009	
			Ne^{++++}	120.18	120.18	
8	7	Ground	N	54.401	54.400	$E_7(Z) = -1.6298Z^2 + 4.4717Z - 5.8432$
			O^+	74.373	74.375	
			F^{++}	97.609	97.609	
			Ne^{+++}	124.10	124.10	
			Na^{++++}	153.86	153.86	

Table A.1 (Continued)

1	2	3	4	5	6	7	8
9	7	$2D$	N O^+ F^{++} Ne^{+++} Na^{++++}	54.296 74.233 97.436 123.90 153.62	54.295 74.235 97.436 123.90 153.62	$E_7(Z) = -1.6301Z^2 + 4.5106Z - 5.9963$	0.22×10^{-2}
10	7	$2P$	N O^+ F^{++} Ne^{+++} Na^{++++}	54.228 74.142 97.323 123.76 153.46	54.227 74.144 97.322 123.76 153.46	$E_7(Z) = -1.6304Z^2 + 4.5385Z - 6.1065$	0.23×10^{-2}
11	8	Ground	O F^+ Ne^{++} Na^{+++} Mg^{++++}	74.809 98.832 126.37 157.42 191.98	74.809 98.834 126.37 157.42 191.98	$E_8(Z) = -1.7562Z^2 + 5.8307Z - 9.0555$	0.24×10^{-2}

Table A.1 (Continued)

1	2	3	4	5	6	7	8
9	7	$2D$	N O^+ F^{++} Ne^{+++} Na^{++++}	54.296 74.233 97.436 123.90 153.62	54.295 74.235 97.436 123.90 153.62	$E_7(Z) = -1.6301Z^2 + 4.5106Z - 5.9963$	0.22×10^{-2}
10	7	$2P$	N O^+ F^{++} Ne^{+++} Na^{++++}	54.228 74.142 97.323 123.76 153.46	54.227 74.144 97.322 123.76 153.46	$E_7(Z) = -1.6304Z^2 + 4.5385Z - 6.1065$	0.23×10^{-2}
11	8	Ground	O F^+ Ne^{++} Na^{+++} Mg^{++++}	74.809 98.832 126.37 157.42 191.98	74.809 98.834 126.37 157.42 191.98	$E_8(Z) = -1.7562Z^2 + 5.8307Z - 9.0555$	0.24×10^{-2}

Table A.1 (Continued)

1	2	3	4	5	6	7	8
12	8	$1D$	O	74.729	74.728	$E_8(Z) = -1.7563Z^2 + 5.8553Z - 9.1645$	0.25×10^{-2}
			F ⁺	98.728	98.731		
			Ne ⁺⁺	126.25	126.25		
			Na ⁺⁺⁺	157.28	157.27		
			Mg ⁺⁺⁺⁺	191.81	191.81		
13	8	$1S$	O	74.611	74.610	$E_8(Z) = -1.7567Z^2 + 5.8957Z - 9.3467$	0.27×10^{-2}
			F ⁺	98.576	98.578		
			Ne ⁺⁺	126.06	126.06		
			Na ⁺⁺⁺	157.06	157.05		
			Mg ⁺⁺⁺⁺	191.56	191.56		
14	9	Ground	F	99.409	99.408	$E_9(Z) = -1.8821Z^2 + 7.3482Z - 13.088$	0.27×10^{-2}
			Ne ⁺	127.82	127.82		
			Na ⁺⁺	160.00	160.00		
			Mg ⁺⁺⁺	195.94	195.94		
			Al ⁺⁺⁺⁺	235.64	236.64		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
15	10	Ground	Ne	128.55	128.55	$E_{10}(Z) = -2.0087Z^2 + 9.0494Z - 18.172$	0.30×10^{-2}
			Na ⁺	161.68	161.68		
			Mg ⁺⁺	198.83	198.83		
			Al ⁺⁺⁺	240.00	240.00		
			Si ⁺⁺⁺⁺	285.18	285.18		
16	11	"	Na	161.86	161.86	$E_{11}(Z) = -2.0666Z^2 + 10.011Z - 21.920$	0.47×10^{-2}
			Mg ⁺	199.37	199.38		
			Al ⁺⁺	241.03	241.03		
			Si ⁺⁺⁺	286.82	286.82		
			P ⁺⁺⁺⁺	336.74	366.74		
17	12	"	Mg	199.61	199.61	$E_{12}(Z) = -2.1241Z^2 + 11.035Z - 26.164$	0.51×10^{-2}
			Al ⁺	241.67	241.68		
			Si ⁺⁺	288.00	287.99		
			P ⁺⁺⁺	338.56	338.56		
			S ⁺⁺⁺⁺	393.37	393.37		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
18	13	Ground	Al	241.88	241.88	$E_{13}(Z) = -2.1822Z^2 + 12.217Z - 31.918$	0.58×10^{-2}
			Si ⁺	288.57	288.58		
			P ⁺⁺	339.64	339.64		
			S ⁺⁺⁺	395.08	395.07		
			Cl ⁺⁺⁺⁺	454.86	454.87		
19	14	"	Si	288.85	288.85	$E_{14}(Z) = -2.2378Z^2 + 13.396Z - 37.781$	0.51×10^{-2}
			P ⁺	340.35	340.35		
			S ⁺⁺	396.33	396.33		
			Cl ⁺⁺⁺	456.79	456.78		
			Ar ⁺⁺⁺⁺	521.71	521.71		
20	14	¹ D	Si	288.81	288.81	$E_{14}(Z) = -2.2378Z^2 + 13.407Z - 37.891$	0.53×10^{-2}
			P ⁺	340.30	340.30		
			S ⁺⁺	396.27	396.27		
			Cl ⁺⁺⁺	456.72	456.71		
			Ar ⁺⁺⁺⁺	521.63	521.63		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
21	14	$1s$	Si P^+ S^{++} Cl^{+++} Ar^{++++}	288.76 340.22 396.17 456.61 521.50	288.75 340.23 396.18 456.60 521.50	$E_{14}(Z) = -2.2384Z^2 + 13.441Z - 38.202$	0.64×10^{-2}
22	15	Ground	P S^+ Cl^{++} Ar^{+++} K^{++++}	340.72 397.17 458.23 523.86 594.08	340.72 397.18 458.22 523.86 594.08	$E_{15}(Z) = -2.2941Z^2 + 14.658Z - 44.412$	0.50×10^{-2}
23	15	$2D$	P S^+ Cl^{++} Ar^{+++} K^{++++}	340.65 397.09 458.12 523.75 593.95	340.65 397.09 458.12 523.74 593.95	$E_{15}(Z) = -2.2939Z^2 + 14.667Z - 44.513$	0.50×10^{-2}

Table A.1 (Continued)

1	2	3	4	5	6	7	8
24	15	2P	P	340.60	340.60	$E_{15}(Z) = -2.2946Z^2 + 14.701Z - 44.832$	0.52×10^{-2}
			S^+	397.03	397.03		
			Cl^{++}	458.05	458.05		
			Ar^{+++}	523.67	523.66		
			K^{++++}	593.86	593.86		
25	16	Ground	S	397.50	397.50	$E_{16}(Z) = -2.3485Z^2 + 15.943Z - 51.390$	0.65×10^{-2}
			Cl^+	459.05	459.05		
			Ar^{++}	525.30	525.31		
			K^{+++}	596.26	596.26		
			Ca^{++++}	671.90	671.90		
26	16	1D	S	397.45	397.45	$E_{16}(Z) = -2.3498Z^2 + 16.004Z - 51.952$	0.56×10^{-2}
			Cl^+	458.98	458.99		
			Ar^{++}	525.23	525.23		
			K^{+++}	596.17	596.17		
			Ca^{++++}	671.81	671.81		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
27	16	$1s$	s	397.37	397.37	$E_{16}(Z) = -2.3480Z^2 + 15.955Z - 51.543$	0.87×10^{-2}
			Cl^+	458.89	458.89		
			Ar^{++}	525.12	525.12		
			K^{+++}	596.05	596.05		
			Ca^{++++}	671.67	671.66		
28	17	Ground	Cl	459.48	459.48	$E_{17}(Z) = -2.4081Z^2 + 17.491Z - 60.873$	0.67×10^{-2}
			Ar^+	526.27	526.28		
			K^{++}	597.89	597.89		
			Ca^{+++}	674.32	674.31		
			Sc^{++++}	755.55	755.56		
29	18	"	Ar	526.82	526.81	$E_{18}(Z) = -2.4617Z^2 + 18.875Z - 68.964$	0.51×10^{-2}
			K^+	599.02	599.02		
			Ca^{++}	676.15	676.15		
			Sc^{+++}	758.21	758.21		
			Ti^{++++}	845.19	845.19		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
30	19	$2D$	Sc ⁺⁺	759.09	759.08	$E_{19}(Z) = -2.5112Z^2 + 20.307Z - 78.106$	0.10×10^{-1}
			Ti ⁺⁺⁺	846.75	846.76		
			V ⁺⁺⁺⁺	939.45	939.45		
			Cr ⁺⁺⁺⁺	1037.2	1037.2		
			Mn ⁺⁺⁺⁺⁺	1139.9	1139.9		
31	20	$3F$	Sc ⁺	759.51	759.50	$E_{20}(Z) = -2.5780Z^2 + 22.613Z - 97.449$	0.12×10^{-1}
			Ti ⁺⁺	847.77	847.74		
			V ⁺⁺⁺	941.14	941.14		
			Cr ⁺⁺⁺⁺	1039.7	1039.7		
			Mn ⁺⁺⁺⁺⁺	1143.4	1143.4		
32	21	$4F$	Ti ⁺	848.19	848.18	$E_{21}(Z) = -2.6401Z^2 + 24.798Z - 115.94$	0.95×10^{-2}
			V ⁺⁺	942.18	942.19		
			Cr ⁺⁺⁺	1041.5	1041.5		
			Mn ⁺⁺⁺⁺	1146.0	1146.0		
			Fe ⁺⁺⁺⁺⁺	1255.9	1255.9		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
33	22	$5D$	V^+	942.67	942.67	$E_{22}(Z) = -2.7012Z^2 + 27.044Z - 135.75$	0.13×10^{-1}
			Cr^{++}	1042.6	1042.6		
			Mn^{+++}	1147.9	1147.9		
			Fe^{++++}	1258.6	1258.6		
			Co^{+++++}	1374.7	1374.7		
34	23	$6S$	Cr^+	1043.1	1043.2	$E_{23}(Z) = -2.7654Z^2 + 29.552Z - 159.51$	0.27×10^{-1}
			Mn^{++}	1149.1	1149.1		
			Fe^{+++}	1260.6	1260.6		
			Co^{++++}	1377.6	1377.6		
			Ni^{+++++}	1500.1	1500.2		
35	24	$5D$	Mn^+	1149.5	1149.5	$E_{24}(Z) = -2.8111Z^2 + 31.211Z - 172.84$	0.14×10^{-1}
			Fe^{++}	1261.7	1261.7		
			Co^{+++}	1379.4	1379.4		
			Ni^{++++}	1502.9	1502.8		
			Cu^{+++++}	1631.9	1631.9		

Table A.1 (Continued)

1	2	3	4	5	6	7	8
36	25	4F	Fe^+ Co^{++} Ni^{+++} Cu^{++++} Zn^{++++}	1262.2 1380.6 1504.8 1634.8 1770.5	1262.1 1380.6 1504.8 1634.8 1770.5	$E_{25}(Z) = -2.8714Z^2 + 33.719Z - 197.77$	0.97×10^{-2}
37	26	3F	Co^+ Ni^{++} Cu^{+++} Zn^{++++}	1381.1 1506.0 1636.8 1773.5	1381.1 1506.0 1636.8 1773.4	$E_{26}(Z) = -2.9248Z^2 + 35.937Z - 219.20$	0.33×10^{-1}
38	27	2D	Ni^+ Cu^{++} Zn^{+++}	1506.6 1638.1 1775.6	1506.6 1638.1 1775.6	$E_{27}(Z) = -3.0894Z^2 + 44.687Z - 335.81$	-

*) See reference 3 in Chapter III.

TABLE A.2

HF Nuclear Magnetic Shielding Values ($\sigma_{\text{HF}} \times 10^5$) for Neutral Atoms and Singly Charged Positive and Negative Ions Calculated Using Energy Polynomials for the Various Isoelectronic Series from $Z = 2$ to $Z = 27$

Z	State	Negative Ions With Charge -1 & At. No. Z-1		Neutral Atoms With At. No. Z		Positive Ions With Charge +1 & At. No. Z+1	
		Present Calculation	Calculation Using Wave Function*	Present Calculation	Calculation Using Wave Function*	Present Calculation	Calculation Using Wave Function*
1	2	3	4	5	6	7	8
2	Ground	2.4399	-	5.9899	5.990	9.5399	9.540
3	"	6.1554	-	10.153	10.145	14.150	14.149
4	"	10.492	10.419	14.936	14.926	19.380	19.381
5	"	15.320	-	20.212	20.199	25.104	25.107
6	"	20.750	20.651	26.090	26.074	31.429	31.430
6	$1D$	20.707	20.578	26.047	26.031	31.387	31.391
6	$1S$	20.643	20.622	25.985	25.965	31.326	31.328
7	Ground	26.778	26.696	32.564	32.547	38.349	38.350

Table A.2 (Continued)

1	2	3	4	5	6	7	8
7	² D	26.715	26.617	32.502	32.484	38.289	38.249
7	² P	26.672	26.562	32.460	32.441	38.248	38.290
8	Ground	33.292	33.205	39.527	39.511	45.762	45.766
8	¹ D	33.251	33.155	39.486	39.468	45.721	45.726
8	¹ S	33.189	33.080	39.426	39.405	45.662	45.667
9	Ground	40.409	40.317	47.091	47.071	53.772	53.775
10	"	48.116	48.021	55.247	55.226	62.378	62.382
11	"	55.595	-	62.932	62.887	70.268	70.271
12	"	63.360	63.150	70.900	70.859	78.441	78.444
13	"	71.277	-	79.024	78.986	86.771	86.774
14	"	79.497	79.328	87.442	87.406	95.386	95.392
14	¹ D	79.478	79.277	87.422	87.383	95.366	95.371
14	¹ S	79.445	79.193	87.392	87.344	95.338	95.330
15	Ground	88.000	87.861	96.144	96.111	104.29	104.292
15	² D	87.974	87.815	96.117	96.078	104.26	104.262
15	² P	87.948	87.779	96.094	96.055	104.24	104.244

Table A.2 (Continued)

1	2	3	4	5	6	7	8
16	Ground	96.760	96.600	105.10	105.044	113.43	113.426
16	1_D	96.721	96.570	105.06	105.022	113.40	113.411
16	1_S	96.712	96.528	105.05	104.989	113.38	113.379
17	Ground	105.73	105.623	114.28	114.262	122.83	122.843
18	"	115.06	114.930	123.80	123.760	132.54	132.540
19	"	124.42	-	133.34	132.934	142.25	141.844
20	"	133.75	133.148	142.90	142.285	152.05	151.957
21	"	143.43	-	152.80	152.134	162.18	162.102
22	"	153.37	152.630	162.96	162.274	172.55	172.500
23	"	163.52	162.812	173.34	172.664	183.16	183.158
24	"	174.13	173.242	184.11	183.650	194.06	193.993
25	"	184.79	183.953	194.99	194.201	205.18	205.099
26	"	195.79	194.798	206.17	205.287	216.56	216.451
27	"	205.83	205.933	216.80	216.635	227.77	228.045

*) See reference 18 in Chapter III.

TABLE A.3

HF Nuclear Magnetic Shielding Values ($\sigma_{\text{HF}} \times 10^5$) for Doubly and Triply Charged Positive and Negative Ions Calculated Using Energy Polynomials for the Various Isoelectronic Series from $Z = 2$ to $Z = 27$

Z	State	Negative Ions		Positive Ions	
		Charge = -3	Charge = -2	Charge = +2	Charge = +3
		At. No. = Z-3	At. No. = Z-2	At. No. = Z+2	At. No. = Z+3
1	2	3	4	5	6
2	Ground	-	-	13.090	16.640
3	"	-	2.1581	18.147	22.145
4	"	1.6044	6.0484	23.824	28.268
5	"	5.5365	10.428	29.996	34.884
6	"	10.072	15.411	36.768	42.107
6	1_D	10.026	15.366	36.728	42.068
6	1_S	9.9593	15.301	36.668	42.010
7	Ground	15.206	20.992	44.135	49.921
7	2_D	15.141	20.928	44.076	49.863
7	2_P	15.096	20.884	44.036	49.824
8	Ground	20.823	27.058	51.996	58.231
8	1_D	20.781	27.016	51.956	58.191
8	1_S	20.717	26.953	51.899	58.135
9	Ground	27.046	33.728	60.454	67.135
10	"	33.854	40.985	69.509	76.640
11	"	40.922	48.259	77.605	84.941

Table A.3 (Continued)

1	2	3	4	5	6
12	Ground	48.278	55.819	85.982	93.522
13	"	55.784	63.530	94.518	102.26
14	"	63.609	71.553	103.33	111.27
14	¹ D	63.589	71.534	103.31	111.26
14	¹ S	63.552	71.499	103.28	111.23
15	Ground	71.711	79.856	112.43	120.58
15	² D	71.687	79.830	112.40	120.55
15	² S	71.656	79.802	112.39	120.53
16	Ground	80.085	88.423	121.77	130.11
16	¹ D	80.037	88.379	121.75	130.09
16	¹ S	80.041	88.376	121.72	130.05
17	Ground	88.637	97.186	131.38	139.93
18	"	97.583	106.63	141.28	150.02
19	"	106.59	115.55	151.17	160.08
20	"	115.45	124.46	161.21	170.36
21	"	124.69	134.06	171.55	180.92
22	"	134.19	143.78	182.14	191.73
23	"	143.89	153.78	192.98	202.79
24	"	154.17	164.15	204.07	214.05
25	"	164.41	176.60	215.37	225.57
26	"	175.02	185.41	226.94	237.32
27	"	183.90	194.87	238.74	249.70

SUMMARY

SUMMARY

Use of Slater free-electron exchange approximation in the Hartree-Fock equations reduces the labour and time for solving them to a considerable extent. Herman and Skillman have been able to perform extensive calculations of the wave functions for the neutral atoms by employing Slater free-electron exchange potential and a "tail correction" to this for creating the potential at large distances from the nucleus. Without such a tail correction the Slater potential goes to zero at large distances which is unphysical. The use of this modification improves over the conventional free-electron exchange approximation. It lowers the energy eigenvalues in general. But the innermost wave functions and their eigenvalues are almost insensitive to the replacement of the conventional averaged exchange potential by the modified averaged exchange potential. The outermost orbitals are only slightly affected whereas the corresponding eigenvalues are appreciably improved. The free-electron exchange approximation, however, fails to correct for the self-coulomb potential at small distances from the nucleus too. Herman and Skillman have not attempted to correct the free-electron exchange potential for such a behaviour. Further, the wave functions obtained by these workers are non-relativistic, single determinantal (both for open-shell and closed-shell systems) and restricted in the sense that their m_s dependence has been ignored.

Keeping the above-mentioned facts in mind an attempt has been made to test the Hartree-Fock-Slater (HFS) wave functions as regards their capability of reproducing those physical properties which require the evaluation of expectation values of certain one-electron operators.

The physical properties chosen to perform the tests on the HFS wave functions are nuclear diamagnetic shielding (σ), diamagnetic susceptibility (χ), Fermi-Contact interaction term (a_0 , the hyperfine splitting constant) and Sternheimer quadrupole antishielding factors (V_∞ and R). It can easily be understood that this choice of the physical properties provides the test both for large and small distances from the nucleus.

It may be remarked here that very recently there have been several developments regarding Slater free-electron exchange approximation, the most interesting of which is to reduce the Slater free-electron exchange potential by a constant multiplicative factor. The effectiveness of such a reduction has been discussed from a comparison of results obtained in the present work on χ and σ using HFS wave functions with those obtained with the reduced potential.

From the calculations of nuclear magnetic shielding and diamagnetic susceptibility values for the rare gas atoms, for which the use of the single determinantal form of the HFS wave functions is quite justified, it has been found that the χ_{HFS} values for these systems are as good as the χ_{HF} values whereas the σ_{HFS} values are found to be uniformly higher than the corresponding σ_{HF} values. It could therefore be concluded that the use of the tail correction really makes the outer-region electron density behave properly and that an inclusion of a correction in the Slater potential for the inner regions also would make the HFS formalism still better. HFS wave functions are actually found to give a higher averaged electron potential at the nucleus which in turn is responsible for the higher values of nuclear magnetic shielding. From a discussion of the results obtained using the available data corresponding

to the reduced Slater exchange potential it is concluded that such a reduced Slater potential can improve the nuclear magnetic shielding values; but it spoils the diamagnetic susceptibility values. It therefore turns out that a uniform reduction of the Slater exchange potential for all the regions is not very helpful. The need for correcting the averaged exchange potential for inner regions as well has been emphasized. Use of relativistic HFS wave functions has been suggested in order to improve upon the nuclear magnetic shielding values especially for large-Z atoms.

Since the single-determinantal form of the HFS wave function is expected to be equally suitable for ions having closed-shell configurations, the HFS wave functions for the isoelectronic series He, Li^+ , Be^{++} , B^{+++} ; F^- , Ne, Na^+ , Mg^{++} , Al^{+++} ; Cl^- , Ar, K^+ , Ca^{++} , Sc^{+++} ; Br^- , Kr, Rb^+ , Sr^{++} , Yt^{+++} ; I^- , Xe, Cs^+ , Ba^{++} , La^{+++} ; At^- , Rn, Fr^+ , Ra^{++} , Ac^{+++} have also been tested by calculating the HFS nuclear magnetic shielding and HFS diamagnetic susceptibility values for them. In these calculations we have, however, used 441-point mesh wave functions in contrast to the 110-point mesh wave functions used in the earlier calculations on rare gas atoms. It has been pointed out that for fast varying functions errors might result by the use of the 110-point mesh. For neutral atoms the 110-point HFS wave functions are available from the book of Herman and Skillman. We obtained the 441-point HFS wave functions by the use of a Herman-Skillman type computer program adopted for the IBM 7044 computer at our Institute. The trend of the χ_{HFS} and σ_{HFS} values for these ions has also been found to be similar to that of χ_{HFS} and σ_{HFS} values for the rare gas atoms. Utilizing the available data for $\sum \langle r^2 \rangle$ in the reduced Slater potential scheme for the case of Li^+ ion we have concluded

in this case as well that the reduced Slater potential does not improve the diamagnetic susceptibility value. In fact it produces $|\chi|$ value which is even higher than the corresponding $|\chi_{\text{HFS}}|$ values, the latter being higher than the corresponding χ_{HF} value. The σ_{HFS} data for the rare gas atoms have been fitted to a fourth-order polynomial, $\sigma_{\text{HFS}}(Z)$, to extrapolate the nuclear magnetic shielding values for other neutral atoms. It has been found that in each isoelectronic series the nuclear magnetic shielding values vary linearly with Z . Nuclear magnetic shielding values for all atoms and ions have been expressed by the empirical relation $\sigma_{\text{HFS}}^{\pm}(Z \pm n) = \sigma_{\text{HFS}}(Z) \pm n\delta_{\pm}(Z)$, where n is the magnitude of the charge on the atom or ion and $\delta_{\pm}(Z)$ are the polynomials giving the variation of shielding with respect to n at a given Z . In particular it has been found that $\delta_{+}(Z) \cong \delta_{-}(Z)$ and that $\delta_{-}(Z)$ is always slightly higher than $\delta_{+}(Z)$ for all isoelectronic series. The above-mentioned relation has been used to extrapolate nuclear magnetic shielding values for the neutral atoms and singly-, doubly- and triply-charged positive and negative ions with $Z = 2$ to $Z = 100$. The extrapolated values have been found to be satisfactory. It has also been pointed out that the extrapolated values can be improved by performing quantum-mechanical calculations of shielding using the HFS wave functions on some more systems so as to provide more number of points for improving upon the fitted polynomials for $\sigma_{\text{HFS}}(Z)$, $\delta_{-}(Z)$ and $\delta_{+}(Z)$. In an attempt to include the directly calculated σ_{HFS} values for doubly- and triply-charged negative ions we tried to obtain HFS wave functions for such ions. After our several unsuccessful attempts to obtain such HFS wave functions we came to the conclusion that the convergence problem in the HFS program is quite serious for negative ions having charges more than one. It has been pointed out that probably this is due to the problem of getting bound states in the HFS model with

the addition of electrons to a given neutral atom. It may be mentioned here, in this connection that even for singly charged negative ions such as F^- the convergence could be obtained after a relatively large number of iterations. From a study of the one-electron $\langle (1/r) \rangle_{HFS}$ integrals it has been concluded that in an atom the mean distance of an electron from the nucleus is not always independent of its angular momentum quantum number.

Based on the concept of stability of SCF wave functions under one-electron perturbations and the Z-expansion for the total energy from the Z-dependent perturbation theory, an alternative method for obtaining nuclear magnetic shielding values for isoelectronic series has been discussed. Total E_{HF}^n values for various isoelectronic series containing two to twentyseven electrons, which have been recently made available from the work of Clementi, could be satisfactorily fitted by means of a polynomial $E_{HF}^n(Z) = A_n Z^2 + B_n Z + C_n$, where n represents the number of the electrons. These polynomials have in turn been used for obtaining σ_{HF}^n values utilizing the relation,

$$\sigma_{HF}^n(Z) = - \frac{\alpha^3}{3} \frac{\partial E_{HF}^n(Z)}{\partial Z}$$

where α represents the fine-structure constant. Since total HFS energy values are not available readily we have not presented similar calculations for σ_{HFS}^n values. It has, however, been found that the HF nuclear magnetic shielding values obtained by the above procedure are almost as good as those obtained by direct quantum-mechanical calculations using the wave functions. It has also been pointed out that the above procedure seems to justify the empirical method which we employed earlier for extrapolating the shielding values for various isoelectronic series.

As a test of the HFS wave functions for open-shell configurations having an unpaired s-electron, hyperfine structure constant, a_c ,

corresponding to the so called Fermi-Contact interaction term has been calculated for the ground states of $\text{Li}(1s^2 2s^1)$, $\text{Na}(1s^2 2s^2 2p^6 3s^1)$, $\text{K}(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1)$, $\text{Cu}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1)$ and $\text{Ca}^+(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1)$ using these wave functions for the respective s valence electrons of these systems. The core-polarization effect which creates nonzero contributions to the fine structure constant a_0 from the paired s-electrons in the s-orbitals of the core, had to be ignored because of the fact that the HFS model does not distinguish between "up" and "down" spin electron wave functions. Thus, the only contribution to a_0 which has been considered here is due to the unpaired s-electron in the valence orbitals of these systems. Unrestricted Hartree-Fock (UHF) scheme, however, takes this into account. It has been found that surprisingly enough the HFS s-wave functions are able to reproduce the experimental values of the constant a_0 better than both HF and UHF wave functions. The agreement between HFS results and experiment is concluded to be fortuitous. From the fact that HFS values of the constant a_0 are regularly higher than the corresponding HF values, it has been pointed out that the agreement between HFS values and the experimental value is, probably, due to the overemphasis of the role of exchange in the HFS formalism. Use of the reduced Slater potential or a correction of the Slater potential in the inner regions as well has been suggested to avoid such an overemphasis.

χ_{HFS} and σ_{HFS} values have also been calculated for neutral atoms having open-shell configurations in three different regions of the Periodic Table. A comparison of these results with the results of available HF calculations revealed that the single-determinantal HFS wave functions are capable of reproducing good values of these constants even for open-shell configurations. This is encouraging in view of the

fact that for open-shell configurations a linear combination of determinantal wave functions is more appropriate than the single determinantal form. However, from these calculations it has again been observed that the HFS formalism consistently leads to an increased value for the potential produced by the electrons of the atomic system at the site of the nucleus in comparison to the HF wave functions. This results in G_{HFS} values which are regularly higher than corresponding G_{HF} values.

Finally, HFS wave functions have also been used to calculate the Sternheimer antishielding factors, γ_{∞} for Na^+ , Cl^- , Al^{+++} , Pr^{+++} , Tm^{+++} , Ce^{+++} , Y^{+++} , In^{+++} , Bi^{+++} and Am^{++} and R for Pr^{+++} , Tm^{+++} and Ce^{+++} utilizing the "perturbation-numerical" approach of Sternheimer. Because of certain limitations of the method of solution the calculated γ_{∞} values are more reliable than the calculated R values. These limitations have been described and it is pointed out that work on the modification of the existing computer program in an effort to remove such limitations is in progress. The detailed results of the present computations have been given in various tables and typical plots of perturbed and unperturbed wave functions have also been presented. It has been found that the HFS wave functions are capable of yielding almost as good estimates of γ_{∞} values for positive ions as those obtained by the use of HF wave functions, utilizing the perturbation-numerical approach. From a detailed comparison of the present results on γ_{∞} with those obtained by others using H or HF wave functions it turns out that the modified form of the free-electron exchange approximation used by Herman and Skillman is only slightly less effective than the actual exchange term of the Hartree-Fock equations in contracting the outer orbitals of the atomic systems. It is pointed out

that a further modification of the Herman-Skillman type Slater free-electron exchange potential at the regions near the nucleus might improve the HFS wave functions.

Taking into account the results of the present HFS investigations on the diamagnetic susceptibility, nuclear magnetic shielding, Fermi-Contact interaction and Sternheimer antishielding factor of atoms and ions as a whole, it is seen that the Slater's approach for the exchange potential offers considerable promise especially with the Herman-Skillman modification for the outer regions. A suitable modification of the exchange potential is necessary for the inner regions as well and when this is done there are good reasons to believe that the results of HFS calculations of several atomic properties will compare very well with those of HF calculations.

PART B

SATURATION IN MULTILEVEL MULTIRESONANCE
ZEEMAN SYSTEMS : A THEORETICAL STUDY

CHAPTER I
INTRODUCTION

CHAPTER I

INTRODUCTION

The distribution of spins in the various Zeeman levels of a system comprising of magnetic nuclei and electrons in the presence of electromagnetic fields which cause transitions between some pairs of levels will be investigated in this part of the thesis.

I.1 MULTILEVEL NATURE OF THE ZEEMAN SYSTEMS

When a system containing magnetic nuclei and unpaired electrons is placed in a magnetic field the interactions between the nuclei and the magnetic field as well as between the electrons and the magnetic field give rise to a set of energy levels^{1,2} which depend on the strength of the magnetic field, the magnetic moments of the electrons and the nuclei and the magnetic quantum numbers of the particles. In addition to this there could be interactions between the nuclei and the electrons which give rise to well-known hyperfine splittings³⁻⁶.

For example, the general Hamiltonian \mathcal{H} for an ion having n electrons (when k -th electron has spin \vec{s}_k and orbital angular momentum \vec{l}_k . \vec{L} and \vec{S} refer to the total orbital and spin angular momentum vectors of the electrons) interacting with a nucleus (having spin \vec{I}) and an external magnetic field \vec{H} can be written as ^{3a},

$$\begin{aligned}
 \mathcal{H} = & \sum_{k=1}^n \left[\frac{p_k^2}{2m} - \frac{Ze^2}{r_k} \right] + \sum_{j>k=1}^n \frac{e^2}{r_{jk}} \quad \left. \begin{array}{l} \text{(Non-relativistic} \\ \text{Hamiltonian)} \end{array} \right\} \begin{array}{l} \text{In absence of} \\ \text{nuclear inter-} \\ \text{actions other} \\ \text{than through a} \\ \text{central electronic} \\ \text{charge} \end{array} \\
 & + V \text{ (electrostatic energy in the field of other} \\
 & \quad \text{lattice charges)} \\
 & + \mathcal{H}_{LS} \text{ (spin-orbit interaction)} \\
 & + \mathcal{H}_{SS} \text{ (Magnetic interaction between electron spins)} \\
 & + \beta \vec{H} \cdot (\vec{L} + 2\vec{S}) \text{ (interaction of electrons with external magnetic field } \vec{H}) \\
 & + 2\gamma\beta\beta_N \sum_{k=1}^n \left\{ \frac{(\vec{l}_k - \vec{s}_k) \cdot \vec{I}}{r_k^3} + \frac{3(\vec{r}_k \cdot \vec{s}_k)(\vec{r}_k \cdot \vec{I})}{r_k^5} + \frac{8\pi}{3} \delta(\vec{r}_k) (\vec{s}_k \cdot \vec{I}) \right\} \\
 & \quad \text{(interaction of nuclear moment with electrons)} \\
 & + \frac{e^2 q}{2I(2I-1)} \sum_{k=1}^n \left\{ \frac{I(I+1)}{r_k^3} - \frac{3(\vec{r}_k \cdot \vec{I})^2}{r_k^5} \right\} \\
 & \quad \text{(interaction between nuclear quadrupole moment and electric} \\
 & \quad \text{field gradient due to the electrons)} \\
 & - \gamma\beta_N \vec{H} \cdot \vec{I} \quad (1.1) \\
 & \quad \text{(interaction of nuclear spin with external magnetic field)}
 \end{aligned}$$

The eigenvalues of the above Hamiltonian give rise to a multilevel Zeeman system. In more complex systems similar multilevel Zeeman systems result.

I.2 STUDY OF MULTILEVEL SYSTEMS

In an experimental investigation of the energy levels of such Zeeman systems as discussed above one usually subjects the assembly of nuclei and electrons to a perturbation by electromagnetic fields in order to see whether there is any interaction between the field and the system at characteristic frequencies (resonances). The frequencies of such resonances depend on the nature of the interactions and generally ranges from radio frequency to optical frequencies. In the absence of the perturbation the various levels are populated in the well-known Boltzmann distribution fashion^{1,3}. This distribution is found to be essentially unaffected even in the presence of weak perturbations. As the strength of the resonant electromagnetic field and hence the strength of the perturbation is increased the populations in the various levels are no longer of the Boltzmann type. To focus our attention let us consider a two-level Zeeman system of an odd electron or a nucleus with spin $I = \frac{1}{2}$ in a magnetic field^{1,7} with energies E_1 and E_2 ($E_2 > E_1$). When the electromagnetic field has the frequency $\nu = (E_2 - E_1)/h$ and has the appropriate polarization it can induce transitions between these levels. In the absence of this transition-inducing electromagnetic field, the population N_i in these two levels is given by the Boltzmann relationship,

$$N_i = A e^{(-E_i/kT)} \quad (1.2)$$

k is the Boltzmann constant and T is the absolute temperature. A is a proportionality factor. Obviously, the population in the lower energy level E_1 is higher. Since the probability of induced absorption is equal to the probability of induced emission ($P_{12} = P_{21}$, where P refers to

the probability of transition due to the applied electromagnetic field, pump) the rate of absorption is initially greater than the rate of emission because of initial excess of population in the lower energy level. It may be noted here that there also exists a process of spontaneous emission by which a transition can occur from the upper level to the lower level. The probability of spontaneous emission depends on the frequency of the electromagnetic field which is applied as the perturbation and it is very small at radio frequencies. The original excess of population in the lower energy level steadily decreases until a stage comes when the populations in both the levels are equal. This phenomenon of equalisation of population between two levels by a pump is called "saturation". Thus if one is observing the absorption, one may find that this is strong when the electromagnetic field is first applied and that it gradually disappears. More generally, however, the absorption settles down to some finite value and it is possible to observe continuous absorption or emission in the presence of the perturbing field. This is because of the fact that apart from the processes of induced emission and absorption there exist various possibilities of radiationless transitions which oppose the equalisation processes and these are familiarly known as "relaxation" processes. A steady-state is usually reached such that the original Boltzmann excess of population in the lower state is altered and continuous absorption or emission may still be observed. If one still wishes to utilize the Boltzmann equation to describe the steady-state population one can do so by using the so-called "spin temperature" concept^{1,8}. Indeed, when the populations in the two levels are equal, the spin

temperature is infinity. The relaxation processes play a very important rôle in governing the population distribution among the various levels. Infact the very establishment of the Boltzmann distribution in the absence of the electromagnetic field perturbation is due to these relaxations^{1,3,9,10}. The relaxations in Zeeman systems can be generally classified as of two types^{1,3,9,10}. These are the spin-lattice and spin-spin relaxations. If one is interested in the study of the dissipation of energy from the spin system, which itself is absorbing energy from the electromagnetic perturbation field, one has to consider the spin-lattice relaxation, since this provides a "leak" from the spin system to the surrounding (lattice) by means of non-radiative transitions. These transitions arise because of the fluctuations in the surrounding which give rise to perturbation fields having a distribution of frequencies⁹. A component of this field could have the characteristic frequency and thus induce transitions of the spins. We could therefore describe these transitions as lattice-induced transitions. In a two-level system it can easily be shown that the probabilities of such transitions or relaxations (R) have the form

$$R_{12} = R_{21} \left[\exp \left\{ -(E_2 - E_1)/kT \right\} \right] \quad (1.3)$$

In general for two pairs of levels m and l we have

$$R_{ml} = R_{lm} \left[\exp \left\{ -(E_l - E_m)/kT \right\} \right] \quad (1.4)$$

When the number of levels increases there is a possibility of having resonances at different frequencies (multiple-resonances). The number of paths that connect a higher energy level

to a lower energy level also increases because now there exists also the possibility of having "cross-relaxations"¹¹ which represent the relaxation of a particular level to another through one or more number of intermediate levels. A cross-relaxation consists of more than one relaxation of the type R_{lm} .

I.3 STEADY-STATE POPULATION DISTRIBUTION IN A MULTILEVEL-MULTIRESONANCE ZEEMAN SYSTEM AND THE RATE EQUATIONS

The study of the steady-state population distribution in multilevel-multiresonance Zeeman systems and in particular the study of the saturation behaviour of these systems can lead to an understanding of the various relaxations and hence of the various interactions in the Zeeman¹²⁻¹⁵ system. The approach employed in the solution of this can be successfully used also in the study of other related problems such as: conditions for population inversion in lasers and masers^{16,17}, Overhauser effect¹⁸, Jeffries-Abragam effect¹⁸ etc.

We shall now consider a β -level Zeeman system containing several lattice-induced relaxation R_{lm} 's and several radiation-induced transitions or pumps P_{rs} 's. We shall investigate the system when steady-state conditions are established in the presence of pumps with frequencies in the radio-frequency region and relaxations. Experimentally this situation is realizable under slow-passage conditions of magnetic resonance spectroscopy⁷. Saturation phenomena are thus amenable to experimental study in magnetic resonance and here one investigates essentially the population distribution of the spins amongst the various levels in the presence of usually strong radiation field (or fields) which induce transition (or transitions) between the given pair (or pairs)

of levels.

We define the normalised populations (Q_i 's) of the spins in the various levels (i 's) as

$$Q_i = \frac{N_i}{N} \quad (i = 1, 2, \dots, \beta)$$

N_i is the number of spins in the i -th level and N represents the total number of spins so that the conservation relation would be

$$N = \sum_{i=1}^{\beta} N_i$$

We shall make the basic assumption that the steady-state population of spins in the various levels is determined by the familiar "rate equations"^{12-14,19}. This assumption can be justified by a consideration of the Boltzmann equation for the density matrix of the system, provided the off-diagonal elements of the density matrix are set equal to zero²⁰⁻²³. Thus in the β -level system considered, the rate equations are,

$$\frac{dQ_m}{dt} = \sum_{l=1}^{\beta'} (Q_l W_{lm} - Q_m W_{ml}) \quad (1.7)$$

($m = 1, 2, \dots, \beta$)

The prime in the summation denotes that $l=m$ is to be omitted. W_{lm} is the total transition probability for a spin in the level l going to level m while W_{ml} is the total transition probability for the reverse process. In the presence of a pump P_{rs} between the levels r and s one may write

$$W_{lm} = R_{lm} + P_{rs} \delta_{rs,lm} \quad (1.8)$$

where

$$\left. \begin{aligned} S_{rs,lm} &= 0 \text{ for } \begin{bmatrix} lm \neq rs \\ \text{or} \\ ml \neq rs \end{bmatrix} \\ &= 1 \text{ for } \begin{bmatrix} lm = rs \\ \text{or} \\ ml = rs \end{bmatrix} \end{aligned} \right\} \quad (1.9)$$

Since in the absence of the pumps the spins attain a Boltzmann distribution, one can note that lattice-induced transition probabilities R_{lm} and R_{ml} are related via the equation (1.4). Due to the principle of microscopic reversibility¹² we have

$$P_{rs} = P_{sr} \quad (1.10)$$

This essentially represents the fact that the r.f. oscillator corresponding to the pump P_{rs} is at infinite temperature so that spontaneous emission could be neglected. The situation will be different of course when optical frequencies are employed, as for example, in lasers. We shall, however, restrict ourselves to r.f. fields for simplicity. The inclusion of spontaneous emission processes in the present treatment does not offer any difficulty.

In magnetic resonance, a useful experimental quantity in relaxation studies employing the saturation procedure is the saturation factor, Z_{rs} , defined as,

$$Z_{rs} = \frac{Q_r(P's) - Q_s(P's)}{Q_r(0) - Q_s(0)} \quad (1.11)$$

where $Q(P's)$ and $Q(0)$ refer to the normalised steady-state population of levels with and without the pumps. For a completely saturated pair of

levels r and s , $Z_{rs} = 0$ while it is equal to unity in the absence of any saturation. Since Z_{rs} is related to the level populations in the above manner it is clear that a study of Z_{rs} can yield information on relaxations. This, however, requires a detailed theoretical analysis of Z_{rs} in terms of various relaxations and pumps. In fact, the present work will be concerned with this aspect of the problem.

The factor Z_{rs} for a pair of levels r and s would be constant only under steady-state conditions which is represented by

$$\frac{dQ_m}{dt} = 0 \quad (m = 1, 2, \dots, \beta) \quad (1.12)$$

With this condition, the rate equations (1.7) reduce to the set of equations

$$\sum_{i=1}^{\beta} (Q_i W_{im} - Q_m W_{mi}) = 0 \quad (1.13)$$

($m=1, 2, \dots, \beta$)

For evaluating Z_{rs} one needs to know Q_i 's which are solutions of the set of equations (1.13) subject to the normalisation condition (eqn. 1.6).

I.4 VARIOUS APPROACHES TO THE SOLUTION OF RATE EQUATIONS

For the solution of the rate equations different authors^{12-14,19} have used various approaches and approximations. One of the approximations employed is that relating to relaxations. In the so-called infinite-temperature approximation^{13,14}, one sets all $R_{lm} = R_{ml}$. Some workers use the high temperature approximation whereby the exponential term of equation (1.4) is linearized in the sense $e^{-x} \simeq 1-x$.

Lloyd and Pake¹² originally discussed the problem of the solution of rate equations in saturation phenomena. These authors were studying the spin relaxations in a six-level Zeeman system arising from the interaction of a nitrogen nucleus (N^{14} , $I=1$) with an odd electron. The sample was an aqueous solution of the free radical, peroxyamine disulphonate ion $ON(SO_3^-)_2$. The electron spin resonance (e.s.r.) spectrum of this free radical exhibits a triplet hyperfine pattern due to the nitrogen and Lloyd and Pake studied the transition $F=3/2, m_F = -3/2 \rightarrow F=3/2, m_F = -1/2$ at 60 Mc/Sec. These authors handled the set of rate equations by forming the appropriate determinant and expanding this in terms of relevant cofactors to obtain the solution for $\Delta_{rs} (=Q_r - Q_s)$. From this analysis Lloyd and Pake were able to interpret their experimental saturation data and discuss the possible dominant relaxation mechanisms in this free radical. The six-level system treated by them had only one pump and the problem did not involve degenerate levels. Their procedure is not easily extended to the case of systems containing many levels and multiple resonances.

An alternative approach can be had by following the suggestion of Bloch²¹. In the infinite-temperature approximation Bloch has shown that the rate equations for the multilevel problem are analogous to Kirchoff's equations for an electrical network. Thus, the solutions to the rate equations in the infinite temperature case can be obtained by employing an electrical analogue. The accuracy of such a procedure is, however, not high.

The procedure of Stephen and Fraenkel¹³ and Stephen¹⁴ also concerns mainly with the infinite-temperature case. This involves the setting up of a transition probability matrix A , whose elements are

given by

$$\left. \begin{aligned} A_{11} &= \sum_{m=1}^{\beta} W_{1m} \\ \text{and } A_{1m} &= -W_{1m} \end{aligned} \right\} \quad (1.14)$$

where, W_{1m} is defined as in equation (1.8). The rate equations in the steady-state (eqn. 1.3) can then be cast into the matrix form

$$\underline{A} \cdot \underline{Q} = 0 \quad (1.15)$$

where, \underline{Q} is a column matrix of Q_i 's. The infinite-temperature approximation used implies all $R_{1m} = R_{m1}$. These authors obtained the solution of the rate equations (1.15) in terms of the cofactors of the matrix \underline{A} . Thus, they obtained the solutions as

$$Q_i = \frac{B_{ii}}{\sum_{k=1}^{\beta} B_{kk}} \quad (i=1,2,\dots,\beta) \quad (1.16)$$

where B_{ii} is the i -th diagonal cofactor of the matrix \underline{A} . In order to obtain these cofactors these authors suggested the "method of diagrams". For this purpose, energy levels are digrammatically represented by "vertices" and relaxation probabilities (R 's) by "lines" joining appropriate "vertices". A minimum set of such diagrams called the "basic diagrams" can be chosen on the basis of "rules" outlined by these authors. Each 'basic diagram' represents a product of certain set of $(\beta-1)$ relaxation probabilities. Each cofactor is then obtained by summing over appropriate 'diagrams' obtained from these 'basic diagrams'. In the infinite-temperature approximation, relaxations between pairs of levels ('vertices') can be

represented by 'lines' but in the finite- and high-temperature cases one should distinguish between "up" and "down" relaxations and hence "arrows" should be used in place of 'lines' to represent the relaxations. The procedure becomes complicated also when the number of levels is large.

Stephen and Fraenkel were able to show the relationship between the saturation factors and the quantities termed saturation parameters which involve the relaxation probabilities R's. In the infinite temperature case in a multilevel system with multiple resonances they could express the saturation factor Z_{rs} in terms of the saturation parameters Ω 's and χ 's. Degeneracies in the levels could also be taken into account. Thus it was shown that

$$Z_{rs}(P_{\alpha\beta}, P_{\gamma\delta}, \dots) = \frac{1 + \sum_{\alpha\beta} P_{\alpha\beta} \chi_{\alpha\beta}^{rs} + \sum_{\alpha\beta\gamma\delta} P_{\alpha\beta} P_{\gamma\delta} \chi_{\alpha\beta,\gamma\delta}^{rs} + \dots}{1 + \sum_{\alpha\beta} P_{\alpha\beta} \Omega_{\alpha\beta} + \sum_{\alpha\beta\gamma\delta} P_{\alpha\beta} P_{\gamma\delta} \Omega_{\alpha\beta,\gamma\delta} + \dots} \quad (1.17)$$

where $P_{\alpha\beta}$, $P_{\gamma\delta}$, are the various applied r.f. fields. Ω 's and χ 's here involve certain types of products of relaxations (R's) and hence have correspondence to the 'diagrams' mentioned above. An explicit expression as that in eqn. 1.17 for Z_{rs} was not given by these authors in the finite-temperature case. However, using the infinite temperature approximation in their method, these authors evaluated the saturation parameters Ω 's in systems having upto ten levels arising out of the interaction between magnetic nuclei and an odd electron. For this purpose they assumed certain forms of the relaxation probabilities (R's) and evaluated various cofactors as polynomials in the parameters appearing in the relaxation probabilities. An explanation for the dependence of the

saturation parameter $\Omega_{\alpha\beta}$ on the nuclear magnetic quantum number m_I observed experimentally for the hyperfine lines in some e.s.r. spectra²⁴ could be also given. The "vertical" transitions in e.s.r. follow the selection rule $\Delta m_S = \pm 1$, $\Delta m_I = 0$ and hence different hyperfine lines correspond to different m_I values. The saturation behaviour of the individual hyperfine lines could be experimentally investigated in favourable cases where there is no overlap of these lines.

The "method of partial distribution" was originally given by Keating, Follis and Barker²⁵ for solving the rate equations for the normalised population distribution in a multilevel Zeeman system. Barker and Keating¹⁶ and Narchal and Barker¹⁸ applied this method to three-level and four-level systems respectively. Keating and Barker¹⁹ have further simplified the procedure and outlined a method which they call "the inspection method" for the purpose of solving the rate equations. Keating and Barker¹⁹ applied it to a four-level system in which they took the linear approximation for R 's. They also applied it to a three-level system without the linear approximation. In general, their method is not limited by any approximations as regards R_{lm} and R_{ml} . The method involves the forming of product combinations of relaxation probabilities R_{lm} 's ($l > m$) and/or P_{rs} ($r < s$) taking a total of $(\beta-1)$ of them in one combination. The "inspection rules"¹⁹ are then employed to select only those combinations which fulfill the criterion therein. The mathematical justification of the 'inspection method' and the 'inspection rules' have been given^{26,27}. This proof uses the theory of linear graphs²⁸ and the matrices associated²⁹ with such graphs. Although Keating and Barker¹⁹ also outlined the utility of their method in obtaining normalised

steady-state population distribution in a multilevel multiresonance Zeeman system, they have not investigated in detail the saturation behaviour and its relation to various relaxation processes in the manner of Stephen and Fraenkel^{13,14}.

Recently Freed²³ has treated the saturation problem by means of density matrix theory, retaining the off-diagonal elements of the density matrix. The density matrix approach of Freed is superior to the rate equation approach for the study of the saturation parameters since no assumption regarding off-diagonal elements in the density matrix need be made. The generalized application of Freed's theory to saturation is, however, very complex. The approach employed by us in this part of the thesis for the theoretical study of the saturation in multilevel-multiresonance Zeeman systems is the rate equation approach. Two reasons may be given here for presenting our work based on the rate equation approach. The first one is the inherent simplicity of the rate equation approach. The second one is that most of the work reported here was completed prior to the publication of Freed's work.

I.5 PRESENT WORK

Although the rate equation approaches of Stephen and Fraenkel^{13,14} and Keating and Barker¹⁹ are apparently dissimilar, the equivalence of these two approaches can be demonstrated. This is dealt with in Chapter II. Since the 'inspection method' for solving the rate equations does not invoke the infinite-temperature approximation, this method can provide a general finite-temperature expression for the saturation factor Z_{rs} in terms of the saturation parameters Ω 's and χ 's. Such an expression has been obtained here and the details are given in Chapter II

where our present expression is compared to that of Stephen and Fraenkel, who however gave the expression for Z_{rs} in the infinite-temperature case only. It may be pointed out here that general expressions for saturation parameters such as obtained here have not been derived earlier elsewhere. Expressions given by Stephen and Fraenkel^{13,14} for the saturation parameters at infinite temperature case are shown to be a particular case of our general expressions. To illustrate the use of our expressions for Ω 's and χ 's calculations of these quantities in a typical four-level system have been made and details presented in Chapter II. The expression obtained for the saturation parameter $\Omega_{\alpha\beta}^{\infty}$ has been also employed to investigate the m_I dependence of the saturation of the hyperfine lines in the e.s.r. spectrum of a multilevel system composed of an odd electron interacting with magnetic nuclei. The results thus obtained are compared with experiments²⁴ and also with the earlier results of Stephen and Fraenkel^{13,14}.

The analysis of the saturation factor and saturation parameters Ω 's and χ 's using the method of Keating and Barker¹⁹ given in Chapter II is well-suited for calculations with a high-speed digital computer. If numerical values of the various relaxations are available one can calculate the saturation parameters in a multilevel-multiresonance system using this analysis. A combination of the available experimental data and the relaxation data can be used along with the above approach to gain further insight into the system. In some cases although numerical values of the relaxations may not be available, their general forms may be obtained on theoretical grounds. To make the computer analysis possible in such cases also the analysis of the saturation factor

and saturation parameters Ω 's and χ 's is further extended to take into account the forms of the various lattice-induced relaxations. This is dealt with in Chapter III. It is hoped that this extension will further help the study of the relaxation mechanisms in general. The method described here has been adopted for machine computations of the various saturation parameters in multilevel-multiresonance Zeeman systems. The salient features of the IBM 7044 computer FORTRAN program written for this purpose are discussed and as examples some results of calculations on a six-level and a ten-level system are presented in Chapter III.

The IBM 7044 computer FORTRAN program is presented in an Appendix.

The summary of this part of the thesis appears at its end.

REFERENCES

1. C.P. Slichter, "Principles of Magnetic Resonance", Harper and Row, New York (1963).
2. N.F. Ramsey, "Nuclear Moments", John Wiley & Sons, New York (1953).
3. A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford (1961).
- 3a. A. Abragam and M.H.L. Pryce, Proc. Roy. Soc. (London), A205, 135 (1951).
4. D.J.E. Ingram, "Free Radicals", Butterworths, London (1958).
5. H.G.B. Casimir, "On Interactions between Atomic Nuclei and Electrons", Teylers Tweede Genootschap, E.F. Bohn, Haarlem (1936).
6. S. Tolansky, "Hyperfine Structure in Line Spectra and Nuclear Spins", Methuen, London (1935).
7. E.R. Andrew, "Nuclear Magnetic Resonance", Cambridge University Press, London (1955).
8. L.C. Hebel, Jr., "Spin Temperature and Nuclear Relaxations in Solids", Advances in Solid State Physics, Academic Press, London (1953) (Eds. F. Seitz and D. Turnbull) Vol. 15, p.409.
9. N. Bloembergen, "Nuclear Magnetic Relaxation", W.A. Benjamin, Inc., New York (1948).
10. C.J. Gorter, "Paramagnetic Relaxation", Elsevier Press, New York (1947).
11. N. Bloembergen, S. Shapiro, P.S. Pershan and J.O. Altman, Phys. Rev., 114, 445 (1959).
12. J.P. Lloyd and G.E. Pake, Phys. Rev., 94, 579 (1954).
13. M.J. Stephen and G.K. Fraenkel, J. Chem. Phys., 32, 1435 (1960).
14. M.J. Stephen, J. Chem. Phys., 34, 484 (1961).
15. H. Shimizu, J. Chem. Phys., 42, 3603 (1965).
16. W.A. Barker and J.D. Keating, Applied Optics, 1, 335 (1962).
17. W.A. Barker and J.D. Keating, "Quantum Electronics" Columbia University Press, New York (1964). (Eds. P. Grivet and N. Bloembergen) Vol. 1, p.741.
18. M.L. Narchal and W.A. Barker, Applied Optics, 2, 787 (1963).

19. J.D. Keating and W.A. Barker, J. Franklin Institute, 274, 253 (1962).
20. R.K. Wangsness and F. Bloch, Phys. Rev., 89, 728 (1953).
21. F. Bloch, Phys. Rev., 102, 104 (1956).
22. A.G. Redfield, IBM J. of Res. and Develop., 1, 19 (1957).
23. J.H. Freed, J. Chem. Phys., 43, 2312 (1965).
24. J.W.H. Schreurs and G.K. Fraenkel, J. Chem. Phys., 34, 756 (1961).
25. J.D. Keating, L.E. Folliis and W.A. Barker, Bull. Am. Phys. Soc. Ser., II, 6, 68 (1961).
26. E.W. Hobbs, J. Franklin Institute, 274, 270 (1962).
27. S. Bedrosian, J. Franklin Institute, 274, 278 (1962).
28. W. Cauer, "Synthesis of Linear Communication Networks", McGraw Hill Book Co., Inc., New York (1958).
29. T. Muir, "A Treatise on Theory of Determinants", Dover Publications, Inc., New York (1960).

CHAPTER II

SATURATION PARAMETERS IN MULTILEVEL -MULTIRESONANCE ZEEMAN SYSTEMS

CHAPTER II

SATURATION PARAMETERS IN MULTILEVEL MULTIRESONANCE ZEEMAN SYSTEMS

II.1 INTRODUCTION

The rate equation approach employed by Keating and Barker in formulating their 'inspection method'¹ for determining steady-state population distribution in multilevel-multiresonance system gives the finite-temperature distribution of spins in the various levels. It has so far not been employed for the study of saturation parameters in such systems. On the other hand Stephen and Fraenkel^{2,3} have given the rate equation approach using 'the method of diagrams' particularly for the study of saturation effects in such multilevel-multiresonance systems. These authors, however, considered the infinite-temperature case only in detail. We shall deal in this Chapter with ^{the} problem of saturation in both finite and infinite temperature cases utilizing an extension of the inspection method, the details of which are given in section 2.

The 'inspection method' and the 'diagram method' are apparently different but if one analyzes in detail the structures of these methods it is found that they are actually equivalent. In section 3 this equivalence will be demonstrated.

Utilizing the finite temperature solution of the rate equations obtained by the 'inspection method' it is possible to present a general finite-temperature expression for the saturation factor Z_{rs} and consequently obtain general finite-temperature expressions for the various saturation parameters Ω 's and χ 's. This is done in section 4. Finite-temperature expressions for the saturation parameters obtained here are also capable of reproducing the infinite-temperature expressions obtained by Stephen³ by properly taking the limits of the former ones. This is demonstrated in section 4.

In section 5, we will be presenting an example of certain typical calculations of finite temperature saturation parameters in a simple four-level electron-nuclear coupled system, which will demonstrate the use of the finite temperature expressions for the saturation parameters obtained in section 4.

A theoretical explanation for the dependence of the saturation of hyperfine lines on the nuclear magnetic quantum number m_I observed in electron spin resonance (e.s.r.) spectra of dilute solutions of free radicals can be obtained by analytically studying the m_I dependence of the saturation parameter Ω_{pq} for the e.s.r. transitions between the pairs of levels 'p and q'. This, however requires the forms of the various relaxations. Following Stephen and Fraenkel^{2,3} these relaxations can be obtained assuming that the relaxation mechanisms (i) anisotropic

intramolecular dipole-dipole interaction and (ii) a cross term between this and g-factor anisotropy are the only mechanisms responsible for producing the differences in the behaviour of the various e.s.r. lines as regards saturation. Expression for the m_I dependence of $\Omega_{pq}(m_I)$ thus obtained in section 6 is compared with experiments⁴ and also with the earlier work of Stephen³.

II.2 OUTLINES OF THE "INSPECTION METHOD" OF KEATING AND BARKER FOR EVALUATING THE NORMALISED STEADY-STATE POPULATION DISTRIBUTION IN A MULTILEVEL-MULTIRESONANCE ZEEMAN SYSTEM

In the 'inspection method' of Keating and Barker¹ for solving the set of rate equations for a β -level system containing several relaxations (conventionally represented by R_{lm} 's with $l > m$) and pumps (conventionally represented by P_{rs} with $r < s$) one first considers all possible combinations of R_{lm} 's and/or P_{rs} 's taking $(\beta-1)$ of them at a time. Then one neglects those combinations which do not fulfill the phenomenology of the rate equations and the normalisation condition. Accordingly, these authors have given the following rules to select the appropriate combinations.

Rules of the Inspection Method

- (i) Discard all those combinations in which all the β levels do not appear as subscripts of R's and/or P's.
- (ii) Discard all those combinations in which any two levels are connected both by a R and a P.

The selected combinations are called allowed 'combinations' or 'terms' and are denoted by X's in general. A particular c-th combination shall be denoted by X_c .

The solutions of the rate equations can be obtained in the form

$$Q_r = \frac{N \sum_{c=1}^n M_c^{(r)} X_c}{\sum_{c=1}^n D_c X_c} \quad (r=1,2,\dots,\beta) \quad (2.1)$$

where n = total number of the allowed combinations, N = total number of spins distributed in the various levels and $M_c^{(r)}$ and D_c are the coefficients of the various 'terms' in the numerator and denominator respectively and these need be evaluated. In order to determine the 'term coefficients' $M_c^{(r)}$ ($r=1,2,\dots,\beta$) for the c -th allowed combination X_c one has to first find the 'intermediate level or levels' in the combination X_c . An 'intermediate level' in a combination is a level which is coupled, by a relaxation R to a higher level, which in turn is coupled to the lowest level. In such a case the term coefficient for the first (lowest) level will be given by

$$M_c^{(1)} = e^{-\Delta E} \quad (2.2)$$

where ΔE is the energy difference between the 'intermediate level' and the higher level through which it is coupled to the first level. There may be however, allowed combinations containing more than one 'intermediate levels'. Thus for a combination having n intermediate levels we have

$$M_c^{(1)} = e^{-\left\{ \sum_{i=1}^n \Delta E_i \right\}} \quad (2.3)$$

where ΔE_i refers to the ΔE value for the i -th intermediate level.

There may also be allowed combinations having no 'intermediate level' and for these $M_c^{(1)} = 1$. Now the other term coefficients $M_c^{(r)}$ ($r=2,3,\dots,\beta$) for the combination X_c can be written easily, since a R_{lm} implies a Boltzmann relation between the populations of the levels l and m whereas P_{rs} implies an equalisation of the populations of the levels r and s . The 'term coefficient' D_c appearing in the denominator is defined as

$$D_c = \sum_{r=1}^{\beta} M_c^{(r)} \quad (2.4)$$

Since the population distribution can be obtained here by inspection of the energy-level diagram of the system the name 'inspection method' was given by the authors.

As regards the proof of this method, it has been given by Hobbs⁵ and this proof is based on the theory of linear graphs⁶ and related matrices and determinants⁷. Bedrosian⁸ has also given some details about the application of linear graph theory to analysis of multilevel systems. It turns out that there is a one-to-one correspondence between the allowed combinations X_c 's and the "Trees" of the linear graph theory considered as a topological problem. In particular, the rules for selecting the allowed combinations of $(\beta-1)$ relaxations are related to the fact that the corresponding 'Tree' has to be an 'R-tree'⁵.

We have for a β -level system a maximum of $G_R(\text{max.})$ relaxations (R_{lm} 's $l > m$) in all. This number is given by

$$G_R(\text{max.}) = \frac{\beta!}{2! (\beta-2)!} \quad (2.5)$$

The maximum possible number $G_P(\text{max.})$ of pumps (P_{rs} 's $r < s$)

will also be equal to $G_R(\text{max.})$ so that $G(\text{max.})$ the total maximum number of relaxations and pumps will be given by

$$\begin{aligned} G(\text{max.}) &= G_R(\text{max.}) + G_P(\text{max.}) \\ &= \beta(\beta-1) \end{aligned} \quad (2.6)$$

Hence the total maximum number $T(\text{max.})$ of combinations to be considered will be given by

$$T(\text{max.}) = \frac{(\beta(\beta-1))!}{(\beta-1)! (\beta(\beta-1) - (\beta-1))!} \quad (2.7)$$

It has been shown by Bedrosian⁸ that out of $T(\text{max.})$ number of possible combinations only $T^*(\text{max.})$ will be "allowed" where

$$T^*(\text{max.}) = (\beta)(\beta-2) \cdot (2)(\beta-1) \quad (2.8)$$

The number $T_R^*(\text{max.})$ of the allowed combinations formed only out of all possible relaxations ($G_R(\text{max.})$ in number) can also be obtained utilizing the results of Bedrosian⁸. It is given by

$$T_R^*(\text{max.}) = (\beta)(\beta-2) \quad (2.9)$$

For cases in which all possible relaxations and pumps are not present the values of G_R and G_P will be less than $G_R(\text{max.})$ and $G_P(\text{max.})$ respectively. Consequently the values of T , T^* and T_R^* will also be less than the corresponding $T(\text{max.})$, $T^*(\text{max.})$ and $T_R^*(\text{max.})$ values.

II.3 EQUIVALENCE OF THE "INSPECTION METHOD" TO THE "DIAGRAM METHOD" OF STEPHEN AND FRAENKEL

As has been pointed out earlier in Chapter I, Stephen and

Fraenkel^{2,3} have mainly treated the infinite-temperature case setting all $R_{lm} = R_{ml}$. In their 'diagram method' they draw diagrams using 'vertices' (which correspond to the levels) and 'lines' (which correspond to relaxations $R_{lm} = R_{ml}$) utilizing the following rules.

Rules of the Diagram Method

- (i) Each diagram must contain all the β vertices and $(\beta-1)$ lines.
- (ii) There must be at least one line attached to each vertex.
- (iii) In each diagram one must be able to go from any one vertex to the rest of the vertices through the lines present in it.
- (iv) Diagrams must have no closed sections.

One can note here that rule (iii) is a consequence of rule (ii) and that rule (iv) is a consequence of rules (i) and (iii).

These rules can easily be seen to be equivalent to the rules of the 'inspection method' given earlier provided one recognises the fact that the vertices and lines of the 'diagram method' correspond respectively to the levels and relaxations of the 'inspection method'. In general, a 'combination' or 'term' of the 'inspection method' corresponds to a 'diagram'. Stephen and Fraenkel actually consider the diagrams made out of R_{lm} 's ($=R_{ml}$'s) only. They call such diagrams as 'basic diagrams'. They further describe several other types of diagrams which one can obtain from the 'basic diagrams'. These are then used by these authors to define various saturation parameters. On the other hand, Keating and Barker¹ discuss all types of combinations simultaneously and do not distinguish between them. This is because these workers were mainly interested in the

solution of the rate equations. In fact, in the present extension of the 'inspection method' to derive general finite-temperature expressions for the various saturation parameters we have considered the various types of combinations separately. Truly speaking the "combinations of the relaxations only" correspond to the "basic diagrams". Stephen³ has shown that for a β -level system if all the relaxations are present, the total number of 'basic diagrams' is $(\beta)(\beta-2)$. This is same as the number of allowed combinations of R's only (see eqn. 2.9). As an example, let us take a four-level system. For this system $\beta=4$ and using equations (2.5) - (2.9) we get,

$$\left. \begin{aligned} G_P(\text{max.}) &= 6 \\ G_R(\text{max.}) &= 6 \\ G(\text{max.}) &= 12 \\ T(\text{max.}) &= 220 \\ T^*(\text{max.}) &= 128 \\ T_R^*(\text{max.}) &= 16 \end{aligned} \right\} \quad (2.10)$$

Table II.1 shows the one-to-one correspondence between all the 16 "basic diagrams" and the 16 "allowed combinations of R's only" in the case of the four-level system quoted above. Fig. II.1 shows the energy-level diagram for this system and in this all the 6 relaxations have been assumed to be present. The reasons for the number of 'basic diagrams' being equal to the number of 'allowed combinations of relaxations' are: (i) Keating and Barker represent conventionally the relaxations as R_{lm} 's with $l > m$ and (ii) Stephen and Fraenkel set all $R_{lm} = R_{ml}$. It should be made clear here that Stephen and Fraenkel set all $R_{lm} = R_{ml}$ to

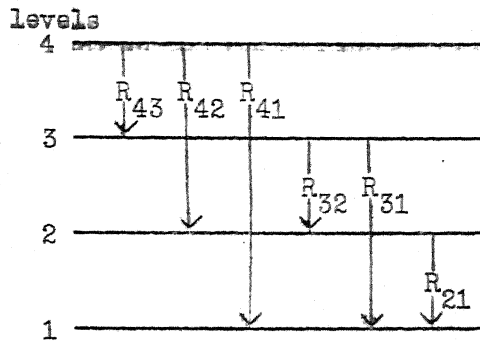


Fig. II.1

A Four-Level System

take the infinite-temperature approximation whereas the convention that $l > m$ in all R_{lm} 's has nothing to do with the infinite-temperature approximation. While finding out the normalised steady-state populations using eqn. (2.1) R_{ml} 's ($m < l$) are actually taken into account through the various term coefficients appearing therein. In the Keating-Barker approach if one considers the infinite-temperature case, $R_{lm} = R_{ml}$. The relaxations now become equivalent to pumps and each 'allowed combination' of these will have all of its term coefficients ($M_c^{(r)}$, $r=1,2,\dots,\beta$) equal to unity.

It must, however, be pointed out that Stephen³ himself has mentioned the possibility of applying the method of diagrams to cases where the infinite-temperature approximation is not employed. In such 'situations' one has to replace the 'lines' in each basic diagram by 'arrows', since the directions of lines should also be now taken into account. Hence, as is clear in Fig. II.2 each line (representing $R_{lm} = R_{ml}$) of a basic diagram should be replaced by either of the two arrows (representing R_{lm} or R_{ml} which are not equal to one another in the finite-temperature case). If this fact is taken into account for each of

the 'lines' appearing in a 'infinite-temperature basic diagram' it is clear that it will give rise to more number of basic diagrams. Thus the number of basic diagrams in the finite-temperature case will be much more

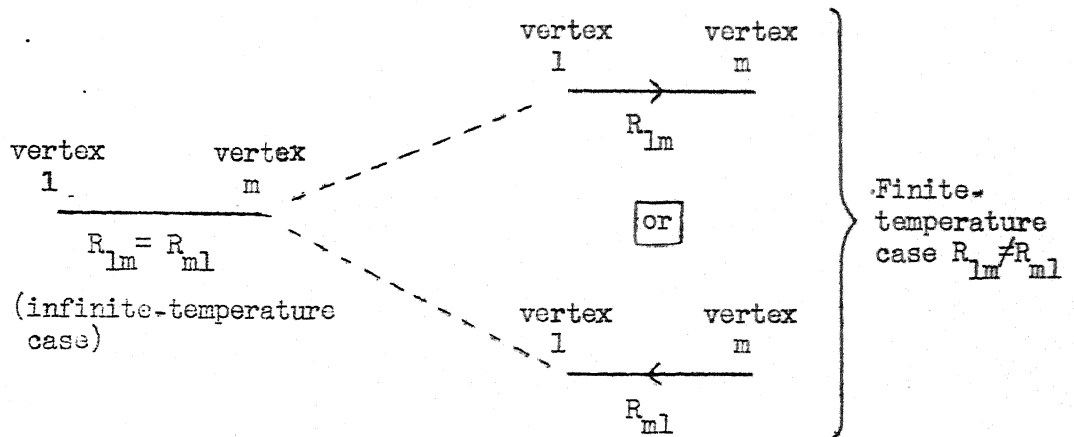


Fig. II.2

than that in the infinite-temperature case. This complicates the situation. However, in the Keating-Barker approach one treats the finite temperature case using the same number of allowed combinations of relaxations as the number of basic diagrams in the Stephen-Fraenkel infinite-temperature approximation. This superiority of the Keating-Barker approach over that of Stephen-Fraenkel approach is a very important point as regards the calculations in the finite-temperature case especially in systems having large number of levels.

II.4 APPLICATION OF THE 'INSPECTION METHOD' OF KEATING AND BARKER FOR THE EVALUATION OF THE SATURATION PARAMETERS

Let us assume that the β -level system contains 't' pumps

$P_{p_{K_1} q_{K_1}}$, $P_{p_{K_2} q_{K_2}}$, ..., $P_{p_{K_t} q_{K_t}}$ between the 't' pairs of levels $p_{K_1} q_{K_1}$, $p_{K_2} q_{K_2}$, ..., $p_{K_t} q_{K_t}$ and certain number of relaxations. The total maximum

Table II.1

Equivalence between "Basic Diagrams" and "Allowed Combinations of Relaxations only" in the Four-Level System.

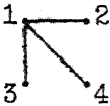
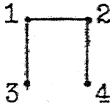
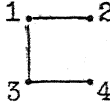
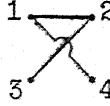
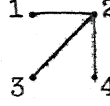
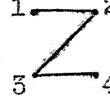
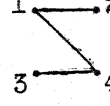
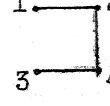
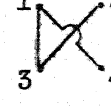
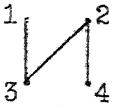
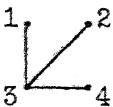
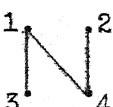
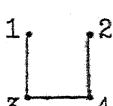
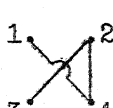
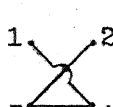
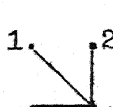
S.No.	Basic Diagram in the Stephen-Fraenkel Approach	Corresponding Allowed Combination of Keating and Barker
1		$R_{21} R_{31} R_{41}$
2		$R_{21} R_{31} R_{42}$
3		$R_{21} R_{31} R_{43}$
4		$R_{21} R_{32} R_{41}$
5		$R_{21} R_{32} R_{42}$
6		$R_{21} R_{32} R_{43}$
7		$R_{21} R_{41} R_{43}$
8		$R_{21} R_{42} R_{43}$
9		$R_{31} R_{32} R_{41}$

Table II.1 (Continued)

10		$R_{31}R_{32}R_{42}$
11		$R_{31}R_{32}R_{43}$
12		$R_{31}R_{41}R_{42}$
13		$R_{31}R_{42}R_{43}$
14		$R_{32}R_{41}R_{42}$
15		$R_{32}R_{41}R_{43}$
16		$R_{41}R_{42}R_{43}$

number of relaxations is $G_R(\text{max.})$ (see eqn. 2.5) but in practice the actual number of relaxations is less than this number, because some of the transitions may not be allowed. For the sake of simplifying the notations we shall henceforth refer to the pumps as $P(1), P(2), \dots, P(t)$ where the subscripts 1, 2, ..., t in the parantheses represent the 't' pairs of levels. Similarly the relaxations shall be represented by $R(i)$'s, each 'i' referring to a pair of levels.

The saturation factor Z_{rs} between the levels 'r' and 's' is given by,

$$Z_{rs} = \frac{Q_r\{P(1), P(2), \dots, P(t)\} - Q_s\{P(1), P(2), \dots, P(t)\}}{Q_r(0) - Q_s(0)} \quad (2.11)$$

where $Q(P(1), P(2), \dots, P(t))$ and $Q(0)$ refer to the normalised steady-state population of the levels with and without the pumps respectively. $Q(0)$'s thus represent the usual Boltzmann distribution and in using equations (2.1) for determining them one has to keep in mind that the X_c 's occurring there in these equations will be the allowed combinations containing only $R(i)$'s. Such combinations shall be called the Boltzmann type of allowed combinations and represented by X_{c1} 's. Let us further assume that the total number of such Boltzmann type of allowed combinations is $n1$. Thus we have,

$$Z_{rs} = \frac{\left\{ \sum_{c=1}^n (M_c^{(rs)} X_c) \right\} / \left\{ \sum_{c1=1}^{n1} (M_{c1}^{(rs)} X_{c1}) \right\}}{\left\{ \sum_{c=1}^n (D_c X_c) \right\} / \left\{ \sum_{c1=1}^{n1} (D_{c1} X_{c1}) \right\}} \quad (2.12)$$

where

$$M_c^{(rs)} = (M_c^{(r)} - M_c^{(s)}) \quad (2.13)$$

The summation over 'c' in equation (2.12) involves all the allowed combinations and that over 'c1' involves only the Boltzmann type of allowed combinations.

The various allowed combinations shall now be divided on the basis of the number of the pumps present in them into various types such as X_{c1} 's, X_{c2} 's,, $X_{c\beta}$'s having no pump, one pump, two pumps,, $(\beta - 1)$ pumps respectively. Let us assume that the total numbers of allowed combinations of these types are n_1, n_2, \dots, n_β respectively. Hence we have

$$n = (n_1) + (n_2) + \dots + (n_\beta) \quad (2.14)$$

Each of these types may further be subdivided into categories on the basis of the specific pump/pumps present in them. This analysis will greatly facilitate the study of the saturation behaviour of the multilevel-multiresonance system. We shall now consider these subdivisions.

X_{c1} 's cannot be further subdivided. X_{c2} 's can be further subdivided into 't' categories such as $X_{c2(1)}$'s, $X_{c2(2)}$'s,, $X_{c2(t)}$'s having the pumps $P(1), P(2), \dots, P(t)$ respectively. Assuming that the total number of combinations of the category $X_{c2(K_1)}$'s is $n_2(K_1)$, we have

$$n_2 = \sum_{K_1=1}^t n_2(K_1) \quad (2.15)$$

X_{c3} 's can be put into categories such as $X_{c3(1,2)}$'s, $X_{c3(1,3)}$'s, , $X_{c3(1,t)}$'s; $X_{c3(2,3)}$'s, $X_{c3(2,4)}$'s, , $X_{c3(2,t)}$'s; $X_{c3(3,4)}$'s, $X_{c3(3,5)}$'s, , $X_{c3(3,t)}$'s; ; $X_{c3(t-1,t)}$'s having the pairs of pumps $P(1)$ and $P(2)$, $P(1)$ and $P(3)$, , $P(1)$ and $P(t)$; $P(2)$ and $P(3)$, $P(2)$ and $P(4)$, , $P(2)$ and $P(t)$; $P(3)$ and $P(4)$, $P(3)$ and $P(5)$, , $P(3)$ and $P(t)$; ; $P(t-1)$ and $P(t)$ respectively. If we assume that the total number of allowed combinations of the category $X_{c3(K_1, K_2)}$ is $n3(K_1, K_2)$ we have

$$n3 = \sum_{K_1 > K_2 = 1}^t n3(K_1, K_2) \quad (2.16)$$

In a similar way we can subdivide the other types also. The $X_{c\beta}$ type of combinations have no relaxations i.e. they are combinations of pumps only. Hence from the above point of view each of them may be thought of as a subdivision. These are as $X_{c\beta(1,2,\dots,\beta-1)}$, $X_{c\beta(2,3,\dots,\beta)}$, $X_{c\beta(3,4,\dots,\beta+1)}$, etc. Assuming that the total number (which is actually unity) of allowed combinations of the category $X_{c\beta(K_1, K_2, \dots, K_{\beta-1})}$ is $n\beta(K_1, K_2, \dots, K_{\beta-1})$ we have

$$n\beta(K_1, K_2, \dots, K_{\beta-1}) = 1 \quad (2.17)$$

(for each set $K_1 > K_2 > \dots > K_{\beta-1}$)

and

$$n\beta = \sum_{\substack{K_1, K_2, \dots, K_{\beta-1} = 1 \\ (K_1 > K_2 > \dots > K_{\beta-1})}}^t n\beta(K_1, K_2, \dots, K_{\beta-1}) \quad (2.18)$$

It can very easily be understood that for the presence of all

such types it is necessary to have at least $(\beta-1)$ pumps in the system. From equation (2.14) and equations of the type (2.15), (2.16) and (2.18) one can write the following summation equation

$$\sum_{c=1}^n = \sum_{c1=1}^{n1} + \sum_{c2=1}^{n2} + \dots + \sum_{c\beta=1}^{n\beta} \quad (2.19)$$

$$\left. \begin{aligned} \sum_{c2=1}^{n2} &= \sum_{K_1=1}^t \sum_{c2(K_1)=1}^{n2(K_1)} \\ \sum_{c3=1}^{n3} &= \sum_{\substack{K_1, K_2=1 \\ (K_1 > K_2)}}^t \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} \\ &\vdots \\ \sum_{c\beta=1}^n &= \sum_{\substack{K_1, K_2, \dots, K_{\beta-1}=1 \\ (K_1 > K_2 > \dots > K_{\beta-1})}}^t \sum_{c\beta(K_1, K_2, \dots, K_{\beta-1})=1}^{n\beta(K_1, K_2, \dots, K_{\beta-1})} \end{aligned} \right\} \quad (2.20)$$

Using equation (2.19) i.e. the division of X_c 's into various types and equation (2.20) i.e. the subdivision of various types into categories in equation (2.12), we get

$$Z_{rs}(P's) = \frac{(A/B)}{(C/D)} \quad (2.21)$$

where

$$B = \sum_{c1=1}^{n1} (M_{c1}^{(rs)} X_{c1}) \quad (2.22a)$$

$$D = \sum_{c1=1}^{n1} D_{c1} X_{c1} \quad (2.22b)$$

$$\begin{aligned} A = & \sum_{c1=1}^{n1} (M_{c1}^{(rs)} X_{c1}) + \sum_{K_1=1}^t \sum_{c2(K_1)=1}^{n2(K_1)} (M_{c2(K_1)}^{(rs)} X_{c2(K_1)}) + \dots \\ & \dots + \sum_{K_1, K_2, \dots, K_{\beta-1}=1}^t \sum_{c\beta(K_1, K_2, \dots, K_{\beta-1})=1}^{n\beta(K_1, K_2, \dots, K_{\beta-1})} (M_{c\beta(K_1, K_2, \dots, K_{\beta-1})}^{(rs)} X_{c\beta(K_1, K_2, \dots, K_{\beta-1})}) \end{aligned} \quad (2.22c)$$

$$\begin{aligned} C = & \sum_{c1=1}^{n1} (D_{c1} X_{c1}) + \sum_{K_1=1}^t \sum_{c2(K_1)=1}^{n2(K_1)} (D_{c2(K_1)} X_{c2(K_1)}) + \dots \\ & \dots + \sum_{K_1, K_2, \dots, K_{\beta-1}=1}^t \sum_{c\beta(K_1, K_2, \dots, K_{\beta-1})=1}^{n\beta(K_1, K_2, \dots, K_{\beta-1})} (D_{c\beta(K_1, K_2, \dots, K_{\beta-1})} X_{c\beta(K_1, K_2, \dots, K_{\beta-1})}) \end{aligned} \quad (2.22d)$$

We now define Y 's as follows

$$Y_{c\eta(K_1, K_2, \dots, K_{\eta-1})} = \frac{X_{c\eta(K_1, K_2, \dots, K_{\eta-1})}}{P(K_1) P(K_2) \dots P(K_{\eta-1})} \quad (2.23)$$

($\eta = 2, 3, \dots, \beta$)

Using equations (2.23) in the equations (2.22c) and (2.22d) we can modify them in forms which are suitable for our purpose. Further, using these modified equations and equations (2.22a) and (2.22b) in equation (2.21) we get

$$Z_{rs} (P(1), P(2), \dots, P(t))$$

$$\begin{aligned}
 & 1 + \sum_{K_1=1}^t P(K_1) \chi_{K_1}^{(rs)} + \sum_{K_1 > K_2=1}^t P(K_1) P(K_2) \chi_{K_1, K_2}^{(rs)} + \dots \\
 & \dots + \sum_{K_1 > K_2 > \dots > K_{\beta-1}=1}^t P(K_1) P(K_2) \dots P(K_{\beta-1}) \chi_{K_1, K_2, \dots, K_{\beta-1}}^{(rs)} \\
 = & \frac{\dots}{1 + \sum_{K_1=1}^t P(K_1) \Omega_{K_1} + \sum_{K_1 > K_2=1}^t P(K_1) P(K_2) \Omega_{K_1, K_2} + \dots} \quad (2.24) \\
 & \dots + \sum_{K_1 > K_2 > \dots > K_{\beta-1}=1}^t P(K_1) P(K_2) \dots P(K_{\beta-1}) \Omega_{K_1, K_2, \dots, K_{\beta-1}}
 \end{aligned}$$

In the above equation Ω 's and χ 's are called the saturation parameters of the spectrum and are defined as below:

$$\begin{aligned}
 \chi_{K_1}^{(rs)} &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} (M_{c2(K_1)}^{(rs)} Y_{c2(K_1)})}{\sum_{c1=1}^{n1} (M_{c1}^{(rs)} X_{c1})} \\
 & \quad (K_1 = 1, 2, \dots, t) \\
 \chi_{K_1, K_2}^{(rs)} &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} (M_{c3(K_1, K_2)}^{(rs)} Y_{c3(K_1, K_2)})}{\sum_{c1=1}^{n1} (M_{c1}^{(rs)} X_{c1})} \\
 & \quad (K_1 = 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2) \\
 & \quad \dots \text{ etc.}
 \end{aligned} \quad (2.25a)$$

$$\left. \begin{aligned}
\Omega_{K_1} &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} (D_{c2(K_1)} Y_{c2(K_1)})}{\sum_{c1=1}^{n1} (D_{c1} X_{c1})} \\
&\quad (K_1 = 1, 2, \dots, t) \\
\Omega_{K_1, K_2} &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} (D_{c3(K_1, K_2)} Y_{c3(K_1, K_2)})}{\sum_{c1=1}^{n1} (D_{c1} X_{c1})} \\
&\quad (K_1 = 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2)
\end{aligned} \right\} (2.25b)$$

General finite-temperature expressions for the saturation parameters such as those given above, have not appeared in the literature so far. However, Stephen³ has derived in the infinite-temperature case, an expression for Z_{rs} which looks similar to the finite-temperature expression (eqn. 2.24) derived here. He has also obtained infinite-temperature expressions for the various saturation parameters Ω 's and χ 's. We shall deduce his infinite-temperature expressions for the saturation parameters Ω 's and χ 's from our general finite temperature expressions (sets of equations (2.25a) and (2.25b)). Before doing so we may comment on the relation between the pumps and the χ 's for a pair of levels 'r and s'.

Since a pump equalizes the populations of the levels which it connects, we have¹ for the combinations X_c 's having P_{rs} in them

$$M_s^{(rs)} = 0 \quad (2.26)$$

and hence if the pair 'r and s' of levels happens to be any one of the pairs of levels connected by the pumps $P(K_1), P(K_2), \dots, P(K_h)$, we get

$$\chi_{K_1, K_2, \dots, K_h}^{(rs)} = 0 \quad (2.27)$$

However, for those cases in which we cannot assume the r.f. oscillator to be at infinite temperature, $P_{sr} \neq P_{rs}$ and equation (2.26) and hence equation (2.27) will not be correct.

Now in the following we shall deal with the 'infinite temperature case' and the 'high temperature case' respectively.

Infinite Temperature Case

We know that $R_{lm} = R_{ml} \left\{ \exp \left((E_l - E_m)/kT \right) \right\}$ and hence if the lattice temperature is infinite $R_{lm} = R_{ml}$. It can be understood from the theory of the 'inspection method' that the various term coefficients are in general exponentials of linear combination of $\Delta E/kT$ where ΔE refers to the $(\beta - 1)$ energy gaps of the β -level system (see sec. 2). As pointed out earlier the non-equality $R_{lm} \neq R_{ml}$, in the finite-temperature case is accounted for through the term coefficients and by defining relaxations as R_{lm} 's ($l > m$). Therefore, in the infinite-temperature case we have for all combinations X_c 's,

$$M_c^{(i)} = 1 \quad (i = 1, 2, \dots, \beta) \quad (2.28)$$

which implies

$$M_c^{(rs)} = 0 \quad (2.29a)$$

$$\text{and} \quad D_c = \beta \quad (2.29b)$$

Using equations (2.29a) and (2.29b) in the sets of equations (2.25a) and (2.25b) we find that in the infinite-temperature case while the saturation parameters χ 's become indeterminate the saturation parameters Ω 's are given by the following equations:

$$\left. \begin{aligned} \Omega_{K_1}^{\infty} &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} (Y_{c2(K_1)})}{\sum_{c1=1}^{n1} (X_{c1})} \\ (K_1 &= 1, 2, \dots, t) \end{aligned} \right\} (2.30)$$

$$\left. \begin{aligned} \Omega_{K_1, K_2}^{\infty} &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} (Y_{c3(K_1, K_2)})}{\sum_{c1=1}^{n1} (X_{c1})} \\ (K_1 &= 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2) \\ &\dots \text{ etc.} \end{aligned} \right\}$$

These expressions for Ω^{∞} 's agree with those derived by Stephen³ using infinite-temperature approximation. He, however, says in his paper that the temperature is high. We shall make a distinction here between high-temperature and infinite-temperature.

The expressions given by Stephen³ for χ 's are for what he refers to as the infinite-temperature case whereas, as we shall see in the following they are actually true in the high-temperature case only.

High Temperature Case

For this case we have $R_{lm} = R_{ml} \left\{ 1 + \left((E_l - E_m)/kT \right) \right\}$ and the saturation parameters are still defined by the sets of equations (2.25a) and (2.25b). One can then utilize the linear approximation for the exponentials occurring in the various term coefficients (and D_c 's) in these sets of equations.

However, we can simplify the expressions for the saturation parameters X 's in this case. For this purpose we consider the categories in the type $X_{c\mu}$. It has the categories $X_{c\mu}(K_1, K_2, \dots, K_{\mu-1})$ ($K_1 = 1, 2, \dots, t$; $K_2 = 1, 2, \dots, t$;; $K_{\mu-1} = 1, 2, \dots, t$ with $K_1 > K_2 > \dots > K_{\mu-1}$). Each of these categories may be further divided

into $(\mu-1)$ species. The ν -th specie for example consists of

$s(u_1, u_2, \dots, u_\nu)r$
 $X_{c\mu}(K_1, K_2, \dots, K_{\mu-1})$'s, namely, the combinations of the category of

$X_{c\mu}(K_1, K_2, \dots, K_{\mu-1})$'s in which the level 's' is connected to the level 'r' via $p_{u_1} - q_{u_1}$, $p_{u_2} - q_{u_2}$, ..., and $p_{u_\nu} - q_{u_\nu}$ in this order and

this path excludes $p_{u_{\nu+1}} - q_{u_{\nu+1}}$, $p_{u_{\nu+2}} - q_{u_{\nu+2}}$, ..., and $p_{u_{\mu-1}} - q_{u_{\mu-1}}$

For $\nu = 1, 2, \dots, \mu-1$ we get the $(\mu-1)$ species. Thus, for $\mu = 2$ which

corresponds to X_{c2} type of combinations, the subdivisions are $X_{c2}(K_1)$

($K_1 = 1, 2, \dots, t$) and from each of these subdivisions we get a single

($\mu-1 = 2-1 = 1$) specie of combinations, namely, those having combinations

$s(u_1)r$
 $X_{c2}(K_1)$'s. For $\mu = 3$ which corresponds to X_{c3} 's, we have the

subdivisions $X_{c3}(K_1, K_2)$ ($K_1 = 1, 2, \dots, t$; $K_2 = 1, 2, \dots, t$ with $K_1 > K_2$)

and from each of these subdivisions we get two species, namely, those

having the combinations $X_{c3(K_1, K_2)}^{s(u_1)r}$'s and those having the combinations $X_{c3(K_1, K_2)}^{s(u_1, u_2)r}$'s and so on.

Let us now introduce the following summation rule

$$\sum_{u_1} X_{c2(K_1)}^{s(u_1)r} = X_{c2(K_1)}^{s(K_1)r} + X_{c2(K_1)}^{s(\bar{K}_1)r} \quad (2.31)$$

As seen here u_1 takes the values K_1 and \bar{K}_1 ; $X_{c2(K_1)}^{s(\bar{K}_1)r}$ is a combination of the category $X_{c2(K_1)}$ in which the level 's' is connected to level 'r' via the path $q_{K_1} - p_{K_1}$ in this order while $X_{c2(K_1)}^{s(K_1)r}$ is a combination of the category $X_{c2(K_1)}$ in which the level 's' is connected to level 'r' via the path $p_{K_1} - q_{K_1}$ in this order. Similarly we introduce the summation

$\sum_{u_1, u_2} X_{c3(K_1, K_2)}^{s(u_1, u_2)r}$ where u_1, u_2 take the values $K_1, \bar{K}_1, K_2, \bar{K}_2$ thus leading to eight terms in all.

Since for all $c1$'s we have $M_{c1}^{(rs)} = (h\nu_{sr})/kT$, we get, using the above-discussed classification of categories into species in the set of equations (2.25a), the following equations for the saturation parameters χ 's in the high temperature case.

$$\chi_{K_1}^{(rs)} = \Omega_{K_1}^{\infty} - \frac{1}{\sum_{c1=1}^{n1} X_{c1}} \left\{ \sum_{u_1} \left(\frac{\nu_{u_1}}{\nu_{sr}} \right) \sum_{c2(K_1)} X_{c2(K_1)}^{s(u_1)r} \right\} \quad (T \text{ high}) \quad (2.32)$$

having the combinations $X_{c3(K_1, K_2)}^{s(u_1)r}$'s and those having the combinations $X_{c3(K_1, K_2)}^{s(u_1, u_2)r}$'s and so on.

Let us now introduce the following summation rule

$$\sum_{u_1} X_{c2(K_1)}^{s(u_1)r} = X_{c2(K_1)}^{s(K_1)r} + X_{c2(K_1)}^{s(\bar{K}_1)r} \quad (2.31)$$

As seen here u_1 takes the values K_1 and \bar{K}_1 ; $X_{c2(K_1)}^{s(\bar{K}_1)r}$ is a combination of the category $X_{c2(K_1)}$ in which the level 's' is connected to level 'r' via the path $q_{K_1} - p_{K_1}$ in this order while $X_{c2(K_1)}^{s(K_1)r}$ is a combination of the category $X_{c2(K_1)}$ in which the level 's' is connected to level 'r' via the path $p_{K_1} - q_{K_1}$ in this order. Similarly we introduce the summation

$\sum_{u_1, u_2} X_{c3(K_1, K_2)}^{s(u_1, u_2)r}$ where u_1, u_2 take the values $K_1, \bar{K}_1, K_2, \bar{K}_2$ thus leading to eight terms in all.

Since for all $c1$'s we have $M_{c1}^{(rs)} = (h\nu_{sr})/kT$, we get, using the above-discussed classification of categories into species in the set of equations (2.25a), the following equations for the saturation parameters χ 's in the high temperature case.

$$\chi_{K_1}^{(rs)} = \Omega_{K_1}^{\infty} - \frac{1}{\sum_{c1=1}^{n1} X_{c1}} \left\{ \sum_{u_1} \left(\frac{\nu_{u_1}}{\nu_{sr}} \right) \sum_{c2(K_1)} X_{c2(K_1)}^{s(u_1)r} \right\} \quad (T \text{ high}) \quad (2.32)$$

$$\chi_{K_1, K_2}^{(rs)} = \Omega_{K_1, K_2}^{\infty}$$

$$\frac{\left[\sum_{u_1} \left\{ \frac{\nu_{u_1}}{\nu_{sr}} \right\} c3(K_1, K_2)^{s(u_1)r} Y_{c3(K_1, K_2)} + \sum_{u_1, u_2} \left\{ \frac{\nu_{u_1} + \nu_{u_2}}{\nu_{sr}} \right\} c3(K_1, K_2)^{s(u_1, u_2)r} Y_{c3(K_1, K_2)} \right]}{\sum_{c1=1}^{n1} \chi_{c1}} \quad (T \text{ high})$$

..... etc. (2.32a)

The Y's in the above equations are defined in general, as follows:

$$Y_{c\mu(K_1, K_2, \dots, K_{\mu-1})}^{s(u_1, u_2, \dots, u_{\mu})r} = \frac{X_{c\mu(K_1, K_2, \dots, K_{\mu-1})}^{s(u_1, u_2, \dots, u_{\mu})r}}{P(K_1)P(K_2) \dots P(K_{\mu-1})} \quad (2.33)$$

Equations similar to the equations (2.32) and (2.32a) have been derived also by Stephen³ using the linear approximation but he has apparently ignored the point that the Ω 's appearing in his equations are essentially Ω^{∞} 's. Thus, in his equations for $\chi_{K_1}^{(rs)}$ (T high), and $\chi_{K_1, K_2}^{(rs)}$ (T high), the linear approximation, $\exp(h\nu/kT) = 1 + (h\nu/kT)$, has not been employed throughout for all the terms. It may be remarked here that as far as the calculations of the saturation parameters χ 's in the high temperature case is concerned there is no additional advantage in using equation (2.32) and equation (2.32a) over the equations (2.25a). However, in practical cases equations such as (2.32) may provide more insight into the physical problems. For example, in electron-nuclear double resonance (ENDOR) experiments where we apply nuclear frequencies

and then study the electron resonance, rs refers to the electron resonance levels and K_1, K_2, \dots etc. refer to nuclear resonance pumps. In these experiments the ratio (ν_{K_1} / ν_{sr}) is very small and hence the second term in equation (2.32) can be neglected so that we get $\chi_{K_1}^{(rs)} = \Omega_{K_1}^{\infty}$

In the case of Overhauser effect one applies the pumps between the electron spin resonance levels K_1, K_2, \dots etc. and studies the populations of the nuclear levels(rs). The ratio (ν_{K_1} / ν_{sr}) , which is of the order of the ratio of the magnetic moments of the electron and nucleus, being large ($\sim 10^3$) the first terms i.e. the $\Omega_{K_1}^{\infty}$ in equation (2.32) is now negligible.

II.5 AN EXAMPLE OF A FOUR LEVEL SYSTEM

To demonstrate the use of our various expressions for the saturation parameters Ω 's and χ 's we shall now present an example of a four-level system and some typical calculations in this system.

We shall take the example of dilute solutions of free radicals for which electron spin resonance (e.s.r.) studies are very common. In the presence of an external magnetic field H_z applied in the z -direction, the Hamiltonian for the free radical system consisting of an unpaired electron interacting with a set of n equivalent nuclei and undergoing motional averaging can be written as^{2,9,10}

$$\mathcal{H} = \beta_e H_z g_e \bar{S}_z - \sum_{k=1}^n \beta_I g_{I_k} H_z I_{z_k} + \sum_{k=1}^n \bar{A}_k (\vec{I}_k \cdot \vec{S}) \quad (2.34)$$

Here β_e is the Bohr magneton; β_I is the nuclear magneton; g_{I_k} is the

nuclear g-factor for the k-th nucleus, \bar{g}_e is the motionally averaged value of the electronic g-tensor ($=\frac{1}{3}(g_{xx}+g_{yy}+g_{zz})$) and \bar{A}_k is the averaged value of the hyperfine interaction for the k-th nucleus. We shall assume here that quadrupole interactions are unimportant. The energy levels corresponding to this Hamiltonian are specified by the m_s and m_I quantum numbers and since the interaction considered here is with a set of equivalent nuclei such that $m_I = \sum_{k=1}^n m_I^k$ we get a set of $2(2m_I+1)$ energy levels in the Paschen-Bach case. The e.s.r. lines correspond to the transitions between Zeeman levels characterized by $\left| (m_s), (m_I) \right\rangle \longrightarrow \left| (m_s+1), (m_I) \right\rangle$.

If we take a single nucleus ($I = \frac{1}{2}$) interacting with an odd electron ($s = \frac{1}{2}$) we get a four-level system. The precise labelling of the four states depends on the relative strength of the nuclear Zeeman term and the hyperfine term and also on the algebraic sign of the nuclear magnetic moment and the hyperfine splitting constant. We shall consider here the scheme in Fig. II.3, taking typical values, such as e.s.r. pump frequency = $\nu_{13} = \nu_{24} = \nu_e = (|\gamma_e|H_z)/2\pi = 30$ kMc, nuclear Zeeman splitting = $\nu_{12} = \nu_{34} = \nu_n = (|\gamma_n|H_z)/2\pi = 15$ Mc.

For an odd electron interacting with n equivalent nuclei (each with spin I) Stephen and Fraenkel² have given, in the extreme motional narrowing case, the forms of various relaxations assuming that the anisotropic intramolecular electron-nuclear dipole-dipole interaction and the g-anisotropy modulation are the dominant mechanisms of intramolecular relaxation.

$$R(\Delta m_s = \pm 1, \Delta m_I = 0) = (K m_I^2 + L m_I + M) \cdot D(n, I, m_I) \quad (2.35a)$$

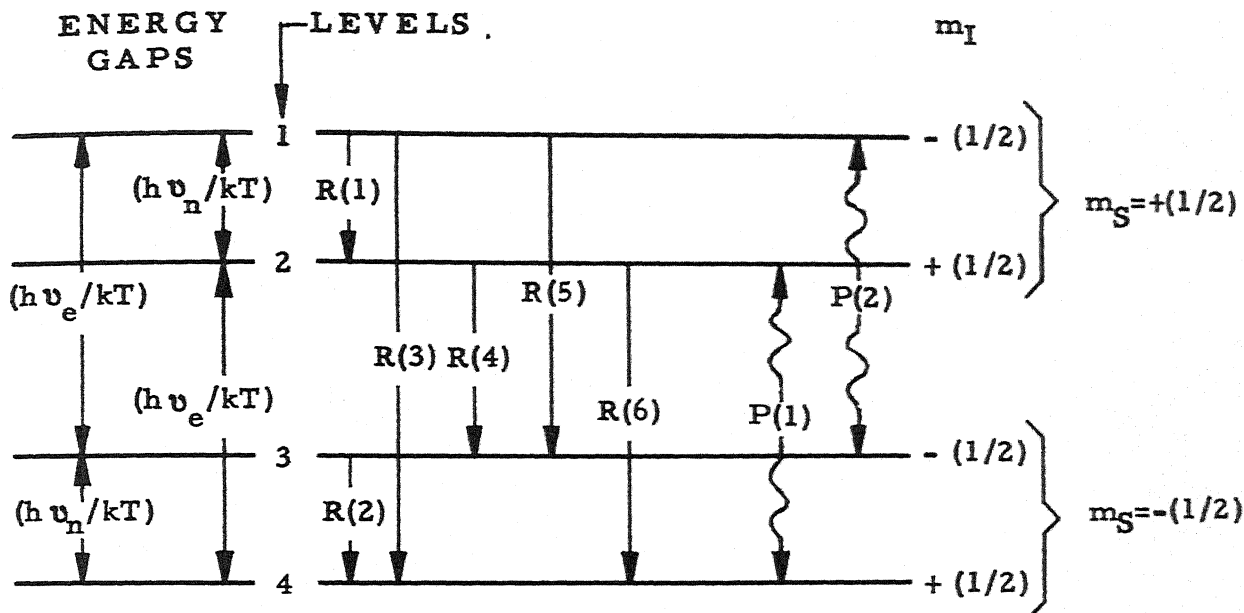


FIG. II. 3 THE ELECTRON-NUCLEAR COUPLED SYSTEM ($S = 1/2$ and $I = 1/2$) FOR WHICH THE SATURATION PARAMETERS ARE CALCULATED. ENERGY LEVELS ARE LABELED BY m_S , m_I VALUES. THE VARIOUS RELAXATIONS ARE SHOWN. THE SYSTEM CONTAINS TWO PUMPS.

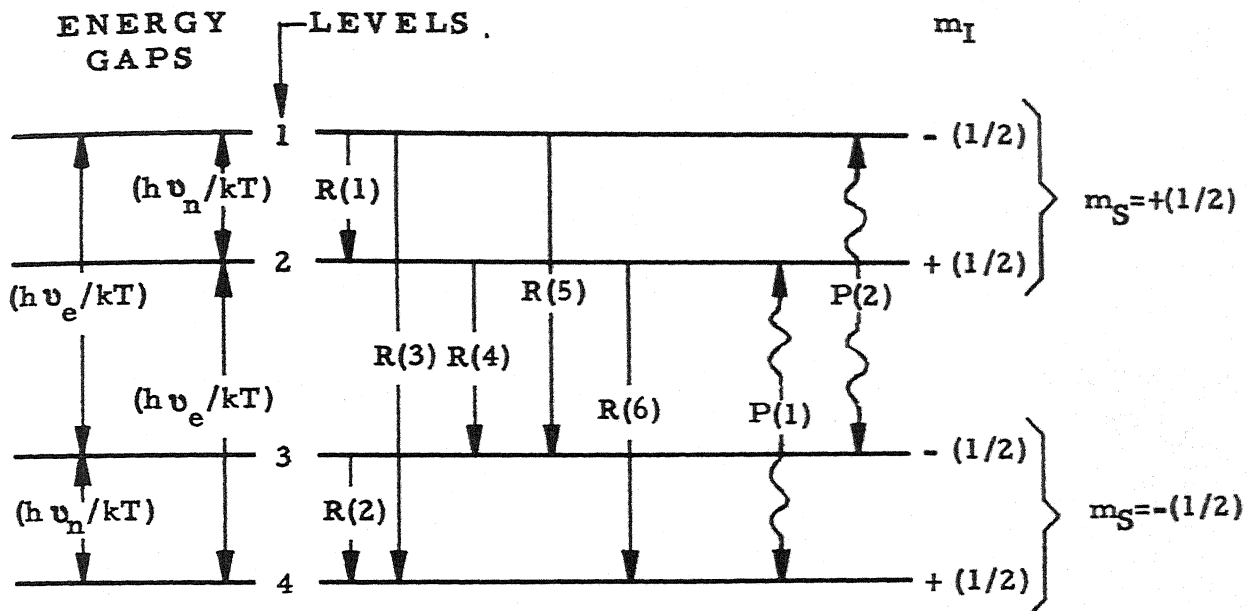


FIG. II. 3 THE ELECTRON-NUCLEAR COUPLED SYSTEM ($S = 1/2$ and $I = 1/2$) FOR WHICH THE SATURATION PARAMETERS ARE CALCULATED. ENERGY LEVELS ARE LABELED BY m_S , m_I VALUES. THE VARIOUS RELAXATIONS ARE SHOWN. THE SYSTEM CONTAINS TWO PUMPS.

$$\begin{aligned}
R(\Delta m_s = \pm 1, \Delta m_I = \pm 1) \\
&= 6R(\Delta m_s = \mp 1, \Delta m_I = \pm 1) \\
&= 4R(\Delta m_s = 0, \Delta m_I = \pm 1) \\
&= nK \sum_{m=-I}^{+I} (I+m)(I+m+1) D(n-1, I, m_I-m) \quad (2.35b)
\end{aligned}$$

$D(n, I, m_I)$ in equations (2.35) refers to the degeneracy of the (m_s, m_I) levels. For an unpaired electron interacting with n equivalent nuclei each having nuclear spin $I = \frac{1}{2}$ we have

$$D(n, \frac{1}{2}, m_I) = \frac{n!}{(\frac{1}{2}n - m_I)! (\frac{1}{2}n + m_I)!} \quad (2.36)$$

K and L are the terms in the matrix elements of the perturbation Hamiltonian $\mathcal{H}'(t)$, corresponding to electron-nuclear dipole-dipole interaction and to the cross term between the g -factor anisotropy and the above dipolar interaction². M consists of the terms of the matrix elements of this Hamiltonian which are independent of m_I . Since our example of four-level system consists of one nucleus ($I = \frac{1}{2}$) interacting with an odd electron ($s = \frac{1}{2}$), we have no degeneracies in our levels. Referring to the Fig. II.3 and utilizing equations (2.35a) and (2.35b) we have

$$\left. \begin{aligned}
 R(1) &= R_{43} = \frac{K}{4} \\
 R(2) &= R_{21} = \frac{K}{4} \\
 R(3) &= R_{41} = \frac{K}{6} \\
 R(4) &= R_{32} = \frac{K}{6} \\
 R(5) &= R_{42} = \frac{K}{4} - \frac{L}{2} + M \\
 R(6) &= R_{31} = \frac{K}{4} + \frac{L}{2} + M
 \end{aligned} \right\} \quad (2.37)$$

Let us assume that two pumps are present (see Fig. II.3)

$$\left. \begin{aligned}
 P(1) &= P_{13} \\
 P(2) &= P_{24}
 \end{aligned} \right\} \quad (2.38)$$

We find from equation (2.24) that the required saturation parameters of the spectrum are $\Omega_1, \Omega_2, \Omega_{2,1}, \chi_1^{(rs)}, \chi_2^{(rs)}$ and $\chi_{2,1}^{(rs)}$. For the numerical evaluation of these parameters we need the values of K, L and M . An order of magnitude estimate of these may be obtained from a consideration of the values calculated by Stephen and Fraenkel² in the case of benzene negative ion. We take their values which are

$$\left. \begin{aligned}
 K &= 3.8 \times 10^3 \text{ sec}^{-1} \\
 L &= -0.8 \times 10^3 \text{ sec}^{-1} \\
 \text{and } M &= 2.42 \times 10^4 \text{ sec}^{-1}
 \end{aligned} \right\} \quad (2.39)$$

Using these, we obtain the following values for the saturation parameters at $T = 300^\circ\text{K}$

$$\Omega_1 = 3.9245 \times 10^{-5} \text{ sec}$$

$$\Omega_2 = 3.8054 \times 10^{-5} \text{ sec}$$

$$\Omega_{2,1} = 1.4934 \times 10^{-9} \text{ sec}^2$$

$$\chi_1^{(34)} = 3.9104 \times 10^{-2} \text{ sec}$$

$$\chi_2^{(34)} = -3.7833 \times 10^{-2} \text{ sec}$$

$$\chi_{2,1}^{(34)} = 1.4859 \times 10^{-9} \text{ sec}^2$$

We may mention here that in this case $[(rs) = (34)]$ the number of various types/categories of combinations are $n1 = 24$, $n2(1) = 8$, $n2(2) = 8$ and $n3(2,1) = 4$.

II.6 AN EXPRESSION FOR THE m_I DEPENDENCE OF THE ELECTRON SPIN RESONANCE LINES OBSERVED IN DILUTE SOLUTIONS OF FREE RADICALS

In the previous section we have discussed in detail the nature of the multilevel problem arising in dilute solutions of free radicals in which an odd electron interacts with a set of equivalent nuclei. The e.s.r. transitions ($| (m_s), (m_I) \rangle \longrightarrow | (m_s \pm 1), (m_I) \rangle$) can be characterized by their m_I values. In the present problem we shall be interested in the saturation parameters $\Omega_{K_1}^\infty$'s where K_1 's refer to the e.s.r. pumps.

The first set of equations given in the sets of equations (2.30) is applicable for the calculation of the saturation parameters

$\Omega_{K_1}^\infty$'s for pairs of levels $p_{K_1} q_{K_1}$'s coupled by the pumps $P_{p_{K_1} q_{K_1}}$'s in the infinite-temperature case. We shall use this expression to derive the m_I dependence for the e.s.r. lines of dilute solutions of free radicals. For simplifying the analysis in this section we shall drop the subscript K_1 in the pair of levels $p_{K_1} q_{K_1}$ and denote the saturation parameter $\Omega_{K_1}^\infty$ by Ω_{pq}^∞ for a pair of levels pq . Thus

$$\Omega_{pq}^\infty = \frac{\sum_{c2(pq)=1}^{n2(pq)} Y_{c2(pq)}}{\sum_{c1=1}^{n1} X_{c1}} \quad (2.40)$$

We shall now assume here that pq in this expression corresponds to an e.s.r. transition. Here $Y_{c2(pq)}$ and X_{c1} contain various relaxations (R 's), which, in the present case are given by equations (2.35a) and (2.35b). The denominator of equation (2.40) can be written as

$$\sum_{c1=1}^{n1} X_{c1} = \sum_{c1'=1}^{n1'} X_{c1'} + \sum_{c1''=1}^{n1''} X_{c1''} \quad (2.41)$$

where $c1'$ refers to those Boltzmann type of combinations which contain the relaxation R_{pq} while $c1''$ refers to those which do not contain this relaxation. Thus $n1 = n1' + n1''$, the total number of combinations of Boltzmann type. In accordance with equation (2.23) and the above definition of the $c1'$ -type of combinations one can write,

$$\sum_{c1'=1}^{n1'} X_{c1'} = R_{pq} \sum_{c2(pq)=1}^{n2(pq)} Y_{c2(pq)} \quad (2.42)$$

since actually n_1' equals $n_2(pq)$. Hence, one can rewrite equation (2.40) as

$$\Omega_{pq}^{\infty} = \frac{\sum_{c_2(pq)=1}^{n_2(pq)} Y_{c_2(pq)}}{R_{pq} \sum_{c_2(pq)=1}^{n_2(pq)} Y_{c_2(pq)} + \sum_{c_1''=1}^{n_1''} X_{c_1''}}$$

or

$$\Omega_{pq}^{\infty} = \frac{1}{R_{pq} + \mathcal{R}} \quad (2.43)$$

where

$$\mathcal{R} = \frac{\sum_{c_1''=1}^{n_1''} X_{c_1''}}{\sum_{c_2(pq)=1}^{n_2(pq)} Y_{c_2(pq)}} \quad (2.44)$$

Since we are interested in the m_I dependence of the saturation between the levels p and q (both having same m_I) based on the above expression for $\Omega_{pq}^{\infty}(m_I)$, it must now be clear in mind that this dependence will come via the forms of the expressions for R_{pq} and the ratio \mathcal{R} .

The m_I dependence of R_{pq} is given in equation (2.35a). As far as the m_I dependence of the ratio \mathcal{R} is concerned we first note that this ratio is of the order of a relaxation. Further, since neither any $X_{c_1''}$ nor any $Y_{c_2(pq)}$ contains the relaxation R_{pq} , the ratio \mathcal{R} will contain the m_I dependence through the relaxations R_{p1} 's and R_{qm} 's all of which will be of the form given in equation (2.35b). The other relaxation

occurring in the ratio \mathcal{R} will be independent of this m_I characterizing the e.s.r. transition in question.

Introducing the form of R_{pq} given in equation (2.35a) in equation (2.43) we get,

$$\Omega_{pq}^{\infty}(m_I) = \frac{1}{(K m_I^2 + L m_I + M) D(m_I) + \mathcal{R}(m_I)}$$

or

$$\Omega_{pq}^{\infty}(m_I) D(m_I) = \frac{1}{(K m_I^2 + L m_I + M) + \mathcal{R}'} \quad (2.45)$$

where

$$\mathcal{R}'(m_I) = \frac{\mathcal{R}(m_I)}{D(m_I)} \quad (2.46)$$

Thus we see that unless the m_I dependence of \mathcal{R}' is known one can not get the exact m_I dependence of Ω_{pq}^{∞} . The task of giving such an exact m_I dependence of Ω_{pq}^{∞} is not simple.

However, if for some reason or the other \mathcal{R}' is negligibly small or else if the m_I dependence through this term is not very dominant from the experimental point of view, we can treat it as a constant which is independent of m_I . Under such an assumption equation (2.45) can be cast into the form

$$\Omega^{\infty}(m_I) D(m_I) = \frac{1}{A m_I^2 + B m_I + C} \quad (2.47)$$

where the constants A, B and C are given by

$$\left. \begin{aligned} A &= K \\ B &= L \\ \text{and } C &= M + R' \end{aligned} \right\} (2.48)$$

Equation (2.47) shows the m_I dependence of Ω^∞ for the e.s.r. saturation in dilute solutions of free radical systems in which the relaxation processes outlined earlier are present and the approximation that R' is independent of m_I is valid. In the case of systems in which processes other than these are significant it is obvious that it is still possible by making use of equation (2.43) to investigate the m_I dependence of Ω^∞ in a similar manner provided the exact forms of the various relaxations for those processes are known.

An expression for the m_I dependence for the case analyzed here has also been given by Stephen³ in the form

$$\Omega_{pq}^\infty(m_I) D(m_I) = A' m_I^2 + B' m_I + C' \quad (2.49)$$

It may be pointed out that Stephen³ also goes through several approximations in order to get the above m_I dependence of Ω_{pq}^∞ . In fact, he completely ignores the m_I dependence which might have come via relaxations other than R_{pq} .

We may note that although the expression given by Stephen³ differs from ours it can be shown that his result is a particular case of our results. To illustrate this point we shall rewrite equation (2.47) as

$$\Omega_{pq}^\infty(m_I) D(m_I) = \frac{\left(\frac{1}{C}\right)}{\left(\frac{A}{C}\right) m_I^2 + \left(\frac{B}{C}\right) m_I + 1}$$

$$= \left(\frac{1}{C}\right) \left[1 + \left\{ \left(\frac{A}{C}\right) m_I^2 + \left(\frac{B}{C}\right) m_I \right\} \right]^{-1} \quad (2.50)$$

Now if

$$\left\{ \left(\frac{A}{C}\right) m_I^2 + \left(\frac{B}{C}\right) m_I \right\} \ll 1 \quad (2.51)$$

then we have from equation (2.50),

$$\begin{aligned} \Omega_{pq}^{\infty}(m_I) D(m_I) &= \left(\frac{1}{C}\right) \left\{ \left(1 - \left(\frac{A}{C}\right) m_I^2 - \left(\frac{B}{C}\right) m_I\right) \right\} \\ &= A' m_I^2 + B' m_I + C' \end{aligned} \quad (2.52)$$

where

$$\left. \begin{aligned} A' &= \frac{(-A)}{(C^2)} \\ B' &= \frac{(-B)}{(C^2)} \\ C' &= \frac{1}{C} \end{aligned} \right\} \quad (2.53)$$

It is seen that unless condition (2.51) is satisfied the above argument will not hold good.

Schreurs and Fraenkel⁴ have attempted a verification of Stephen's expression for the m_I dependence of Ω^{∞} in para-benzosemiquinone ion. From the line-width and peak-height measurements they were able to show experimentally that,

$$\frac{1}{D(m_I) \Omega(m_I)} = \left\{ (0.027) m_I^2 + (-0.011) m_I + (0.690) \right\} \quad (2.54)$$

We see that in this free radical system $[D(m_I) \Omega(m_I)]^{-1}$ has the form $a m_I^2 + b m_I + c$ whereas according to Stephen $[D(m_I) \Omega(m_I)]$

and not $[D(m_I)\Omega(m_I)]^{-1}$ should have the above form. Our expression (eqn. 2.47) shows, however, that $[D(m_I)\Omega(m_I)]^{-1}$ itself has the form $a m_I^2 + b m_I + c$. Hence, our expression for the m_I dependence appears to be directly verified by the experimental results of Schreurs and Fraenkel⁴. The experimental results may be also taken to indicate that \mathcal{R} in equation (2.46) is, to a good approximation, independent of m_I .

II.7 CONCLUSION

Two rate-equation approaches, namely (1) the 'Diagram method' of Stephen and Fraenkel and (2) the 'Inspection method' of Keating and Barker for obtaining the steady-state population distribution in a multilevel-multiresonance Zeeman systems are discussed and shown to be equivalent. The 'inspection method' has been extended to the calculation of various saturation parameters in the general finite temperature case by suitably analysing the general finite-temperature expression for the saturation factor Z_{rs} . Infinite-temperature expressions for the saturations parameters given by Stephen are shown to be deducible from our general finite-temperature expressions for the corresponding saturation parameters. For the calculation of saturation parameters it is found that our procedure can be adopted simultaneously for the finite, high and infinite temperature cases with the same amount of effort, whereas in Stephen's approach, if one goes from the infinite-temperature case to the finite- or high-temperature case one has to consider numerous additional diagrams. The usefulness of our finite-temperature expressions for the saturation parameters has been demonstrated by taking an example of a simple four-level electron-nuclear coupled system and presenting some typical results for this.

The dependence of the saturation parameter Ω_{pq}^{∞} on nuclear magnetic quantum number m_I for the hyperfine lines in the e.s.r. spectra of dilute solutions of free radicals has been discussed. The two mechanisms, anisotropic intramolecular dipole-dipole interaction and the g-anisotropy modulation, are the only type of relaxations assumed to be responsible for such an m_I dependence. The results thus obtained agree with available experimental data. An earlier expression derived by Stephen for the m_I dependence of Ω_{pq}^{∞} is shown to be a particular form of our expression. Since such a m_I dependence contains in it various relaxation parameters, an experimental study correlated with theory may yield valuable information regarding these relaxation processes.

Using our general finite-temperature expressions for the various saturation parameters and the rules of the inspection method one can utilize high-speed digital computers for such calculations. This, however, will require numerical values for the various relaxations (R 's) present in the multilevel-multiresonance system in question. Generally, such numerical values are not available but the forms of these relaxations may be known in terms of certain parameters which characterize the relaxation mechanisms present in the system. Hence, before attempting to adopt the present extension of the 'inspection method' for machine computation of the saturation parameters it will be useful to extend this analysis further in order to take into account the forms of the various relaxations. Such an extension will be presented in the next Chapter where we will also adopt the final form of the method to machine computation of the saturation parameters.

REFERENCES

1. J.D. Keating and W.A. Barker, J. Franklin Inst., 274, 253 (1962).
2. M.J. Stephen and G.K. Fraenkel, J. Chem. Phys., 32, 1435 (1960).
3. M.J. Stephen, J. Chem. Phys., 34, 484 (1961).
4. J.W.H. Schreurs and G.K. Fraenkel, J. Chem. Phys., 34, 756 (1961).
5. E.W. Hobbs, J. Franklin Inst., 274, 270 (1962).
6. W. Cauer, "Synthesis of Linear Communication Networks", Mc-Graw Hill Book Co., Inc., New York (1958).
7. T. Muir, "A Treatise on the Theory of Determinants", Dover Publications, Inc., New York (1960).
8. S. Bedrosian, J. Franklin Inst., 274, 278 (1962).
9. A. Carrington and H.C. Longuet-Higgins, Mol. Phys., 5, 447 (1962).
10. J.H. Freed, J. Chem. Phys., 43, 2312 (1965).

CHAPTER III

MACHINE COMPUTATION OF SATURATION PARAMETERS IN MULTILEVEL MULTIFESONANCE ZEEMAN SYSTEMS

CHAPTER III

MACHINE COMPUTATION OF SATURATION PARAMETERS IN MULTILEVEL- MULTIRESONANCE ZEEMAN SYSTEMS*

III.1 INTRODUCTION

In the previous chapter the "inspection method"¹ of Keating and Barker for the solution of the rate equations to determine the finite-temperature steady-state population distribution was applied to multilevel-multiresonance Zeeman systems and starting with the expression for the saturation factor Z_{rs} between a pair of levels r and s , general finite-temperature expressions were obtained for the various saturation parameters Ω 's and χ 's. In the present Chapter we further extend the 'inspection method' to take into account the explicit forms of the various relaxations, product combinations of which occur in the expressions for the various saturation parameters. The relaxations will be, in general, functions of certain parameters which characterize the various relaxations.

* A paper based on the material presented in this Chapter has been accepted for publication in the Journal of The Franklin Institute.

mechanisms present in the system. Therefore, the present analysis is believed to allow to go deeper into the relaxation mechanisms through the saturation studies. For simplicity we, however, assume that various relaxations are linear combinations of a number of relaxation parameters which characterize various relaxation mechanisms present in the system. Utilizing such forms for the relaxations, the expressions for the saturation parameters derived in Chapter II are modified. We discuss this in section 2.

The final form of the 'inspection method' thus obtained is adopted for machine computations of the saturation parameters in a multiresonance case of a multilevel system having certain predominant relaxation mechanisms which govern the relaxation parameters discussed above. Section 3 deals with a discussion of the salient features of the computer program. For such calculations in fairly large level systems, the use of a high speed digital computer is very helpful and seems to be essential.

In section 4 we give the results of our calculations on a six-level and a ten-level system. These two examples considered here are similar to those treated earlier by Stephen and Fraenkel^{2,3}, but our calculations are more rigorous.

III.2 FURTHER MODIFICATION OF THE EXPRESSIONS FOR THE SATURATION PARAMETERS

In Chapter II the expression for the saturation factor Z_{rs} between the levels r and s in a J -level system having t pumps $P(1)$, $P(2)$,, $P(t)$ between the various t pairs of levels $p_{K_1} q_{K_1}$,

$P_{K_2}^{q_{K_2}}, \dots, P_{K_t}^{q_{K_t}}$ has been put in the form

$$\begin{aligned}
 & 1 + \sum_{K_1=1}^t P(K_1) \chi_{K_1}^{rs} + \sum_{K_1 > K_2=1}^t P(K_1) P(K_2) \chi_{K_1, K_2}^{rs} + \dots \\
 & \dots + \sum_{K_1 > K_2 \dots > K_{\beta-1}=1}^t P(K_1) P(K_2) \dots P(K_{\beta-1}) \chi_{K_1, K_2, \dots, K_{\beta-1}}^{rs} \\
 Z_{rs} = & \frac{\dots + \sum_{K_1 > K_2 \dots > K_{\beta-1}=1}^t P(K_1) P(K_2) \dots P(K_{\beta-1}) \chi_{K_1, K_2, \dots, K_{\beta-1}}^{rs}}{1 + \sum_{K_1=1}^t P(K_1) \Omega_{K_1} + \sum_{K_1 > K_2=1}^t P(K_1) P(K_2) \Omega_{K_1, K_2} + \dots} \\
 & \dots + \sum_{K_1 > K_2 \dots > K_{\beta-1}=1}^t P(K_1) P(K_2) \dots P(K_{\beta-1}) \Omega_{K_1, K_2, \dots, K_{\beta-1}}
 \end{aligned} \tag{3.1}$$

Here the saturation parameters Ω 's and χ 's are defined (see Chapter II) as follows:

$$\begin{aligned}
 \Omega_{K_1} &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} D_{c2(K_1)} Y_{c2(K_1)}}{\sum_{c1=1}^{n1} D_{c1} X_{c1}} \\
 (K_1 &= 1, 2, \dots, t) \\
 \Omega_{K_1, K_2} &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} D_{c3(K_1, K_2)} Y_{c3(K_1, K_2)}}{\sum_{c1=1}^{n1} D_{c1} X_{c1}}
 \end{aligned} \tag{3.2a}$$

($K_1 = 1, 2, \dots, t$; $K_2 = 1, 2, \dots, t$ with $K_1 > K_2$)
and similar expressions for $\Omega_{K_1, K_2, K_3}, \Omega_{K_1, K_2, K_3, K_4}, \dots$ etc.

$$\begin{aligned}
\chi_{K_1}^{rs} &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} M_{c2(K_1)}^{(rs)} Y_{c2(K_1)}}{\sum_{c1=1}^{n1} M_{c1}^{(rs)} X_{c1}} \\
(K_1 &= 1, 2, \dots, t)
\end{aligned}$$

$$\begin{aligned}
\chi_{K_1, K_2}^{rs} &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} M_{c3(K_1, K_2)}^{(rs)} Y_{c3(K_1, K_2)}}{\sum_{c1=1}^{n1} M_{c1}^{(rs)} X_{c1}} \\
(K_1 &= 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2)
\end{aligned}
\tag{3.2b}$$

and similar expressions for $\chi_{K_1, K_2, K_3}^{rs}, \chi_{K_1, K_2, K_3, K_4}^{rs}, \dots$ etc.

As in Chapter II, we have in above equations

$$\begin{aligned}
Y_{c2(K_1)} &= \frac{X_{c2(K_1)}}{P(K_1)} \\
Y_{c3(K_1, K_2)} &= \frac{X_{c3(K_1, K_2)}}{P(K_1)P(K_2)} \\
&\dots\dots\dots \text{etc.}
\end{aligned}
\tag{3.3}$$

Now, let us assume that the various relaxations are given as linear combinations of 'l' parameters $L(1), L(2), \dots, L(l)$ characterizing the various relaxation mechanisms in the system under consideration. In other words, we have, for example,

relaxation $R(i)$ is given by

$$R(i) = \sum_{j=1}^1 B(ij) L(j) \quad (3.4)$$

$B(ij)$ is a matrix of 'relaxation coefficients'. The (i) in $R(i)$ is used here simply to count the relaxations and each (i) refers to a pair of levels. It may be pointed out that in equation (3.4) the various subscripts are written in parentheses only because such procedure and notation is useful in computer programming. This procedure will therefore be adopted henceforth. Also, much of the analysis ~~that follows~~ has been presented in such a manner as to facilitate the programming of α computer.

For a β -level system the total maximum number of relaxations is

$G_{R(\max.)} = \left\{ (\beta)! \right\} / \left\{ (2)! (\beta-2)! \right\}$. In equation (3.4) (i) can thus take values $1, 2, \dots, G_{R(\max.)}$. In practice the number of relaxations is usually less than $G_{R(\max.)}$ because some of the transitions may not be allowed. If all the relaxations present in the system have the form (3.4) it may be easily understood that, each X_{c1} being a product of certain $(\beta-1)$ relaxations is a polynomial of degree $(\beta-1)$ in the parameters $L(j)$'s. Hence, in general,

$$X_{c1} =$$

$$\sum_{i_1=1}^1 \sum_{i_2=i_1}^1 \dots \sum_{i_{\beta-1}=i_{\beta-2}}^1 \text{ALPHA}_{c1}(i_1, i_2, \dots, i_{\beta-1}) L(i_1) L(i_2) \dots L(i_{\beta-1}) \quad (3.5a)$$

Similarly, each $Y_{c2(K_1)}$ being a product of $(\beta-2)$ relaxations is a polynomial of degree $(\beta-2)$ in $L(j)$'s and in general

$$Y_{c2(K_1)} = \sum_{i_1=1}^1 \sum_{i_2=i_1}^1 \dots \sum_{i_{\beta-2}=i_{\beta-3}}^1 \text{ALPHA}_{c2(K_1)}(i_1, i_2, \dots, i_{\beta-2}) L(i_1)L(i_2) \dots L(i_{\beta-2}) \quad (3.5b)$$

Each $Y_{c3(K_1, K_2)}$ being a product of $(\beta-3)$ relaxations is hence a polynomial of degree $(\beta-3)$ in $L(j)$'s and we have

$$Y_{c3(K_1, K_2)} = \sum_{i_1=1}^1 \sum_{i_2=i_1}^1 \dots \sum_{i_{\beta-3}=i_{\beta-4}}^1 \text{ALPHA}_{c3(K_1, K_2)}(i_1, i_2, \dots, i_{\beta-3}) L(i_1)L(i_2) \dots L(i_{\beta-3}) \quad (3.5c)$$

and so on.

In equations (3.5) ALPHA's are the coefficients of the various terms of the respective polynomials and are obviously products or sums of the products of appropriate $B(ij)$ coefficients, e.g.

$\text{ALPHA}_{c\eta(K_1, K_2, \dots, K_{\eta-1})}(i_1, i_2, \dots, i_{\beta-\eta})$ is the coefficient of the term $L(i_1)L(i_2) \dots L(i_{\beta-\eta})$ in a $(\beta-\eta)$ order polynomial of the product of certain $(\beta-\eta)$ relaxations.

Since in the digital computer we cannot ordinarily handle variables of more than three dimensions in a simple manner, each set of i 's in each order polynomial is numbered and thus designated by a variable NTERM,

$$\text{NTERM} = \text{NTERM}(i_1, i_2, \dots, i_{\beta-\eta}) \quad (3.6)$$

In fact, we perform the summations in equations of the type (3.5) exhausting the summations always from the inner side, and set $NTERM = 1$ for the first term ($i_1=1, i_2=1, \dots, i_{\beta-h-1}=1, i_{\beta-h}=1$), $NTERM = 2$ for the second term ($i_1=1, i_2=1, \dots, i_{\beta-h-1}=1, i_{\beta-h}=2$), \dots , $NTERM = 1$ for the l -th term ($i_1=1, i_2=1, \dots, i_{\beta-h-1}=1, i_{\beta-h}=1$), $NTERM = (1 + 1)$ for the $(1 + 1)$ -th term ($i_1=1, i_2=1, \dots, i_{\beta-h-2}=1, i_{\beta-h-1}=2, i_{\beta-h}=2$), $NTERM = (1 + 2)$ for the $(1 + 2)$ -th term ($i_1=1, i_2=1, \dots, i_{\beta-h-2}=1, i_{\beta-h-1}=2, i_{\beta-h}=3$), \dots , $NTERM = (2l - 1)$ for the $(2l - 1)$ -th term ($i_1=1, i_2=1, \dots, i_{\beta-h-2}=1, i_{\beta-h-1}=2, i_{\beta-h}=1$), $NTERM = 2l$ for the $2l$ -th term ($i_1=1, i_2=1, \dots, i_{\beta-h-2}=1, i_{\beta-h-1}=3, i_{\beta-h}=3$) and so on.

Now, coming to the set $L(i_1)L(i_2)\dots L(i_{\beta-h})$ of the parameters $L(j)$'s, one can easily understand that

$$\begin{aligned} L(i_1)L(i_2)\dots L(i_{\beta-h}) &= L(1)^{LP(NTERM,1)} L(2)^{LP(NTERM,2)} \dots L(1)^{LP(NTERM,1)} \\ &= \prod_{j=1}^1 L(j)^{LP(NTERM,j)} \end{aligned} \quad (3.7)$$

where $NTERM$ corresponds to the set $i_1, i_2, \dots, i_{\beta-h}$ in the $(\beta-h)$ order polynomial and $LP(NTERM, j)$ is the power of $L(j)$ in this $NTERM$ -th term of the polynomial.

In view of these notational simplifications

$ALPHA_{c\eta}(K_1, K_2, \dots, K_{\eta-1})$ is the coefficient of the $NTERM$ -th term i.e., the term which corresponds to

$$\{L(1)\}^{LP(NTERM,1)} \{L(2)\}^{LP(NTERM,2)} \dots \{L(1)\}^{LP(NTERM,1)} \text{ in the}$$

$(\beta - \eta)$ order polynomial obtained by a product of certain $(\beta - \eta)$ relaxations.

Equations (3.5) will then appear as follows

$$X_{c1} = \sum_{NTERM=1}^{MTERM} c1 \text{ ALPHA}_{c1} (NTERM) \prod_{j=1}^1 L(j)^{LP(NTERM,j)} \quad (3.8a)$$

$$Y_{c2(K_1)} = \sum_{NTERM=1}^{MTERM} c2 \text{ ALPHA}_{c2(K_1)} (NTERM) \prod_{j=1}^1 L(j)^{LP(NTERM,j)} \quad (3.8b)$$

$$Y_{c3(K_1, K_2)} = \sum_{NTERM=1}^{MTERM} c3 \text{ ALPHA}_{c3(K_1, K_2)} (NTERM) \prod_{j=1}^1 L(j)^{LP(NTERM,j)} \quad (3.8c)$$

where $MTERM_{c1}$, $MTERM_{c2}$, $MTERM_{c3}$, etc. are the number of terms in the polynomials of the type X_{c1} , $Y_{c2(K_1)}$, $Y_{c3(K_1, K_2)}$, etc. respectively. These numbers depend on the number '1' of the relaxation parameters. We shall use these numbers later. It is worth mentioning here that if we made product of N relaxations of the type (3.4) having '1' parameters each using the first principles, we encounter $(1)^N$ pseudo-terms but the actual number of terms in the product will be less than this number.

In a β -level system we have $(\beta - 1)$ independent energy gaps namely $E_2 - E_1 = \zeta(1) = E_{12}$, $E_3 - E_2 = \zeta(2) = E_{23}$, etc. and it can be easily understood from the theory of the inspection method¹ that various term-coefficients are in general exponentials of linear combinations of these energy gaps. Hence, we have

$$M_c^{(r)} = \exp \left\{ \sum_{j=2}^{\beta} A_c(r, j) \frac{\zeta(j-1)}{kT} \right\} \quad (r = 1, 2, \dots, \beta) \quad (3)$$

k being the Boltzmann constant and T the absolute temperature. $\xi(j-1)$ is the energy gap ($E_j - E_{j-1}$) appearing in the linear combination with the numerical coefficient $A_c(r, j)$ in the r -th term-coefficient of the c -th allowed combination. Note that we have not used the value 1 (one) for the index (j) in the above equation (3.9). This will help us in future analysis as we will see a little later. Using equation (3.9) in the definitions of D_c and $M_c^{(rs)}$ (see Chapter II) we get,

$$D_c = \sum_{i=1}^{\beta} \left[\exp \left\{ \sum_{j=2}^{\beta} A_c(i, j) \frac{\xi(j-1)}{kT} \right\} \right] \quad (3.10)$$

and

$$M_c^{(rs)} = \left[\exp \left\{ \sum_{j=2}^{\beta} A_c(r, j) \frac{\xi(j-1)}{kT} \right\} - \exp \left\{ \sum_{j=2}^{\beta} A_c(s, j) \frac{\xi(j-1)}{kT} \right\} \right] \quad (3.11)$$

Using equations (3.8) and equation (3.10) in equations (3.2a) we get,

$$\left. \begin{aligned} \rho_{-K_1} &= \frac{x_1(K_1)}{y} \\ (K_1=1, 2, \dots, t) \\ \Omega_{K_2, K_1} &= \frac{x_2(K_1, K_2)}{y} \\ (K_1=1, 2, \dots, t; K_2=1, 2, \dots, t \text{ with } K_1 > K_2) \\ &\dots \dots \dots \text{etc.} \end{aligned} \right\} \quad (3.12a(i))$$

where

$$y = \sum_{c1=1}^{n1} (y'_{c1}) (y''_{c1}) \quad (3.12a(ii))$$

with

$$\left. \begin{aligned} y'_{c1} &= \sum_{i=1}^{\beta} \exp \left\{ \sum_{j=2}^{\beta} A_{c1}(i,j) \frac{\xi(j-1)}{kT} \right\} \\ y''_{c1} &= \sum_{NTERM=1}^{MTERM} c1 \text{ ALPHA}_{c1}(NTERM) \prod_{j=1}^1 (L(j))^{LP(NTERM,j)} \end{aligned} \right\} (3.12a(ii))$$

and

$$\left. \begin{aligned} x1(K_1) &= \sum_{c2(K_1)=1}^{n2(K_1)} (x1'(K_1)) \cdot (x1''(K_1)) \\ (K_1 &= 1, 2, \dots, t) \\ x2(K_1, K_2) &= \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} (x2'(K_1, K_2)) \cdot (x2''(K_1, K_2)) \\ (K_1 &= 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2) \\ &\dots \dots \dots \text{etc.} \end{aligned} \right\} (3.12a(iii))$$

with

$$\left. \begin{aligned} x1'(K_1) &= \sum_{i=1}^{\beta} \exp \left\{ \sum_{j=2}^{\beta} A_{c2(K_1)}(i,j) \frac{\xi(j-1)}{kT} \right\} \\ x1''(K_1) &= \sum_{NTERM=1}^{MTERM} c2 \text{ ALPHA}_{c2(K_1)}(NTERM) \prod_{j=1}^1 (L(j))^{LP(NTERM,j)} \end{aligned} \right\} (3.12a(iii))$$

and

$$\left. \begin{aligned}
 x2'(K_1, K_2) &= \sum_{i=1}^{\beta} \exp \left\{ A_{c3}(K_1, K_2)(i, j) \frac{\xi(j-1)}{kT} \right\} \\
 x2''(K_1, K_2) &= \sum_{NTERM=1}^{MTERM} c3 \text{ ALPHA } c3(K_1, K_2)^{(NTERM)} \prod_{j=1}^1 (L(j))^{LP(NTERM, j)} \\
 &\dots \text{ etc.}
 \end{aligned} \right\} (3.12a(iii))$$

Similarly we may write the expressions for the saturation parameters

χ 's as

$$\left. \begin{aligned}
 \chi_{K_1}^{rs} &= \frac{z1^{(rs)}(K_1)}{y^{(rs)}} \\
 &(K_1=1, 2, \dots, t) \\
 \chi_{K_2, K_1}^{rs} &= \frac{z2^{(rs)}(K_1, K_2)}{y^{(rs)}} \\
 &(K_1=1, 2, \dots, t; K_2=1, 2, \dots, t \text{ with } K_1 > K_2) \\
 &\dots \text{ etc.}
 \end{aligned} \right\} (3.12b(i))$$

where,

$$y^{(rs)} = \sum_{c1=1}^{\beta} (y_{c1}^{(rs)}) (y_{c1}^{''}) \quad (3.12b(ii))$$

with

$$y_{c1}^{(rs)} = \exp \left\{ \sum_{j=2}^{\beta} A_{c1}(r, j) \frac{\xi(j-1)}{kT} \right\} - \exp \left\{ \sum_{j=2}^{\beta} A_{c1}(s, j) \frac{\xi(j-1)}{kT} \right\} \quad (3.12b(iii))$$

and

$$\left. \begin{aligned}
 z1^{(rs)}(K_1) &= \sum_{c2(K_1)=1}^{n2(K_1)} (z1^{(rs)}(K_1)) (x1^n(K_1)) \\
 (K_1 &= 1, 2, \dots, t) \\
 z2^{(rs)}(K_1, K_2) &= \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} (z2^{(rs)}(K_1, K_2)) (x2^n(K_1, K_2)) \\
 (K_1 &= 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2) \\
 &\dots\dots\dots \text{etc.}
 \end{aligned} \right\} (3.12b(iii))$$

with

$$z1^{(rs)}(K_1) = \exp \left\{ \sum_{j=2}^{\beta} A_{c2(K_1)}(r, j) \frac{\xi(j-1)}{kT} \right\} - \exp \left\{ \sum_{j=2}^{\beta} A_{c2(K_1)}(s, j) \frac{\xi(j-1)}{kT} \right\} \quad (3.12\bar{b}(iii))$$

$$\begin{aligned}
 z2^{(rs)}(K_1, K_2) &= \exp \left\{ \sum_{j=2}^{\beta} A_{c3(K_1, K_2)}(r, j) \frac{\xi(j-1)}{kT} \right\} \\
 &- \exp \left\{ \sum_{j=2}^{\beta} A_{c3(K_1, K_2)}(s, j) \frac{\xi(j-1)}{kT} \right\} \quad (3.12\bar{b}(iii)) \\
 &\dots\dots\dots \text{etc.}
 \end{aligned}$$

The problem becomes still further simplified when the various energy gaps $\xi(j)$'s are small compared to kT and thus the linear (high temperature) approximation $\exp(\xi(j)/kT) = (1 + \xi(j)/kT)$ can be made. Thus equation (3.9) in this case becomes,

$$M_c^{(r)} = 1 + \sum_{j=2}^{\beta} A_c(r, j) \frac{\xi(j-1)}{kT} \quad (3.1)$$

If we define

$$\left. \begin{aligned} A_c(r,1) &= 1 \\ (\text{for all } r \text{ and } c) \\ \text{and } \xi(0)/kT &= 1 \end{aligned} \right\} (3.14)$$

we can rewrite equation (3.13) as

$$M_c^{(r)} = \sum_{j=1}^{\beta} A_c(r,j) \frac{\xi(j-1)}{kT} \quad (3.15)$$

Equation (3.15) is in a form which is suitable for computational purposes.

We now have,

$$\begin{aligned} D_c &= \sum_{i=1}^{\beta} M_c^{(i)} = \sum_{i=1}^{\beta} \sum_{j=1}^{\beta} A_c(i,j) \frac{\xi(j-1)}{kT} \\ &= \sum_{j=1}^{\beta} \sum_{i=1}^{\beta} A_c(i,j) \frac{\xi(j-1)}{kT} \\ &= \sum_{j=1}^{\beta} A_c(\beta+1,j) \frac{\xi(j-1)}{kT} \end{aligned} \quad (3.16)$$

where

$$A_c(\beta+1,j) = \sum_{i=1}^{\beta} A_c(i,j) \quad (3.17)$$

Now, we define a single variable MPAIR to designate a pair 'rs' of the levels such as

$$\text{MPAIR} = \text{MPAIR}(rs) \quad (3.18)$$

The various relaxations are given by equation (3.4) with a set of values of the relaxation coefficients $B(ij)$'s and the saturation

parameters can be calculated using the following equations (3.19a) and (3.19b) which are the ones obtained by using the above-mentioned linear approximation in equations (3.12a) and (3.12b) respectively,

$$\Omega_{K_1} = \frac{\sum_{NTERM=1}^{MTERM} c2 \left[\sum_{j=1}^{\beta} XD^{c2(K_1)}(NTERM, j) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{LP(NTERM, i)} \right]}{\sum_{NTERM=1}^{MTERM} c1 \left[\sum_{j=1}^{\beta} XD^{c1}(NTERM, j) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{LP(NTERM, i)} \right]}$$

$$(K_1 = 1, 2, \dots, t)$$

$$\Omega_{K_2, K_1} = \frac{\sum_{NTERM=1}^{MTERM} c3 \left[\sum_{j=1}^{\beta} XD^{c3(K_1, K_2)}(NTERM, j) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{LP(NTERM, i)} \right]}{\sum_{NTERM=1}^{MTERM} c1 \left[\sum_{j=1}^{\beta} XD^{c1}(NTERM, j) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{LP(NTERM, i)} \right]}$$

$$(K_1 = 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2)$$

..... etc.

$$\chi_{K_1}^{\text{MPAIR}} = \frac{\sum_{\text{NTERM}=1}^{\text{MTERM}} c_2 \left[\sum_{j=1}^{\beta} \text{XNR}^{c_2(K_1)}(\text{NTERM}, j, \text{MPAIR}) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{\text{LP}(\text{NTERM}, i)} \right]}{\sum_{\text{NTERM}=1}^{\text{MTERM}} c_1 \left[\sum_{j=1}^{\beta} \text{XNR}^{c_1}(\text{NTERM}, j, \text{MPAIR}) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{\text{LP}(\text{NTERM}, i)} \right]}$$

$$(K_1 = 1, 2, \dots, t; \text{MPAIR} = 1, 2, \dots, \text{NPAIR})$$

$$\chi_{K_1, K_2}^{\text{MPAIR}} =$$

$$\sum_{\text{NTERM}=1}^{\text{MTERM}} c_3 \left[\sum_{j=1}^{\beta} \text{XNR}^{c_3(K_1, K_2)}(\text{NTERM}, j, \text{MPAIR}) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{\text{LP}(\text{NTERM}, i)} \right]$$

$$\sum_{\text{NTERM}=1}^{\text{MTERM}} c_1 \left[\sum_{j=1}^{\beta} \text{XNR}^{c_1}(\text{NTERM}, j, \text{MPAIR}) \frac{\xi(j-1)}{kT} \right] \left[\prod_{i=1}^1 \{L(i)\}^{\text{LP}(\text{NTERM}, i)} \right]$$

$$(K_1 = 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2; \text{MPAIR} = 1, 2, \dots, \text{NPAIR})$$

..... etc.

(3.19b)

In these equations (3.19a) and (3.19b) XD's and XNR's are two-dimensional and three-dimensional variables respectively and are defined as follows:

$$\begin{aligned}
XD^{c1}(NTERM, j) &= \sum_{c1=1}^{n1} A_{c1}(\beta+1, j) \text{LAPHA}_{c1}(NTERM) \\
XD^{c2(K_1)}(NTERM, j) &= \sum_{c2(K_1)=1}^{n2(K_1)} A_{c2(K_1)}(\beta+1, j) \text{ALPHA}_{c2(K_1)}(NTERM) \\
XD^{c3(K_1, K_2)}(NTERM, j) &= \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} A_{c3(K_1, K_2)}(\beta+1, j) \text{ALPHA}_{c3(K_1, K_2)}(NTERM) \\
&\dots\dots\dots \text{etc.}
\end{aligned}
\tag{3.20a}$$

and

$$\begin{aligned}
XNR^{c1}(NTERM, j, \text{MPAIR}(rs)) &= \sum_{c1=1}^{n1} \{A_{c1}(r, j) - A_{c1}(s, j)\} \text{ALPHA}_{c1}(NTERM) \\
XNR^{c2(K_1)}(NTERM, j, \text{MPAIR}(rs)) &= \sum_{c2(K_1)=1}^{n2(K_1)} \{A_{c2(K_1)}(r, j) - A_{c2(K_1)}(s, j)\} \text{ALPHA}_{c2(K_1)}(NTERM) \\
XNR^{c3(K_1, K_2)}(NTERM, j, \text{MPAIR}(rs)) &= \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} \{A_{c3(K_1, K_2)}(r, j) - A_{c3(K_1, K_2)}(s, j)\} \text{ALPHA}_{c3(K_1, K_2)}(NTERM) \\
&\dots\dots\dots \text{etc.}
\end{aligned}
\tag{3.20b}$$

It may be mentioned here that $\chi_{K_1, K_2, \dots, K_n}^{\text{MPAIR}}$ becomes zero (see Chapter II) if MPAIR happens to correspond to pairs of levels

which are connected by any one of the pumps $P(K_1), P(K_2), \dots, P(K_h)$.

In the infinitely high temperature case when $\exp(\epsilon(j)/kT) = 1$, the saturation parameters χ 's are not defined (see Chapter II) and the saturation parameters Ω 's are given as Ω^∞ 's by the following equations:

$$\left. \begin{aligned} \Omega_{K_1}^\infty &= \frac{\sum_{c2(K_1)=1}^{n2(K_1)} Y_{c2(K_1)}}{\sum_{c1=1}^{n1} X_{c1}} \\ (K_1 &= 1, 2, \dots, t) \\ \Omega_{K_2, K_1}^\infty &= \frac{\sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} Y_{c3(K_1, K_2)}}{\sum_{c1=1}^{n1} X_{c1}} \\ (K_1 &= 1, 2, \dots, t; K_2 = 1, 2, \dots, t \text{ with } K_1 > K_2) \\ &\dots\dots\dots \text{etc.} \end{aligned} \right\} (3.21)$$

Putting the explicit forms of Y 's and X_{c1} (equations (3.8)) in the equations (3.21) and rearranging we get,

$$\begin{aligned}
\Omega_{K_1}^{\infty} &= \frac{\sum_{NTERM=1}^{MTERM} c2 \left[\text{BETA}^{c2(K_1)}(NTERM) \right] \left[\prod_{j=1}^1 \{L(j)\}^{LP(NTERM,j)} \right]}{\sum_{NTERM=1}^{MTERM} c1 \left[\text{BETA}^{c1}(NTERM) \right] \left[\prod_{j=1}^1 \{L(j)\}^{LP(NTERM,j)} \right]} \\
\Omega_{K_1, K_2}^{\infty} &= \frac{\sum_{NTERM=1}^{MTERM} c3 \left[\text{BETA}^{c3(K_1, K_2)}(NTERM) \right] \left[\prod_{j=1}^1 \{L(j)\}^{LP(NTERM,j)} \right]}{\sum_{NTERM=1}^{MTERM} c1 \left[\text{BETA}^{c1}(NTERM) \right] \left[\prod_{j=1}^1 \{L(j)\}^{LP(NTERM,j)} \right]} \\
&\dots\dots\dots \text{etc.}
\end{aligned} \tag{3.22}$$

where BETA's are one-dimensional variables defined as

$$\begin{aligned}
\text{BETA}^{c1}(NTERM) &= \sum_{c1=1}^{n1} \text{ALPHA}_{c1}(NTERM) \\
\text{BETA}^{c2(K_1)}(NTERM) &= \sum_{c2(K_1)=1}^{n2(K_1)} \text{ALPHA}_{c2(K_1)}(NTERM) \\
\text{BETA}^{c3(K_1, K_2)}(NTERM) &= \sum_{c3(K_1, K_2)=1}^{n3(K_1, K_2)} \text{ALPHA}_{c3(K_1, K_2)} \\
&\dots\dots\dots \text{etc.}
\end{aligned} \tag{3.23}$$

In sets of equations (3.19a) and (3.19b) the numerators and denominators are polynomials of various degrees in the parameters $L(j)$'s

with linear combinations of the energy gaps $\epsilon(j)$'s as the coefficients, whereas in equations (3.22) the numerators and denominators are polynomials of various degrees in the parameters $L(j)$'s with numerical coefficients.

III.3 THE COMPUTER PROGRAM

Based on the sets of equations (3.20a), (3.20b) and (3.23) a computer program has been written in the FORTRAN language⁴ for electronic digital computers (specifically for the IBM 7044 with 32 K memory). Since it is not possible here to discuss the entire program in detail, the present description is confined to a brief discussion of the salient points only.

The program consists of a main program 'SAT' and three subroutines namely (i) Subroutine 'SELECT' (ii) Subroutine 'ILAAIJ' and (iii) Subroutine 'ALGEBR'. We shall now describe these one by one.

The Main Program 'SAT'

The main program first reads NCAL, the number of the systems to be analysed in a single run and takes the systems one by one (DO LOOP JCAL = 1, NCAL) for analysis. For a particular system taken, it reads NLEVEL, KRELAX, NPUMP, MCAL, MPUMP1, MPUMP2, NPARA, NPAIR. NLEVEL, KRELAX and NPUMP are the number of the levels, the total number of the relaxations and the total number of the pumps in the system. NCAL is a controlling datum. If MCAL=1, the calculations are to be done (using equations (3.23)) in the infinitely high temperature case only but if MCAL=2, the calculations are to be done (using equations (3.20a), (3.20b) and (3.23)) both in the finite temperature case with linear

approximation and in the infinitely high temperature case. MPUMP1 and MPUMP2 are the two limits characterizing the types of the combinations to be considered and hence the types of the saturation parameters to be evaluated, e.g. if MPUMP1 = 1 and MPUMP2 = 3, the combinations to be considered are X_{c1} , X_{c2} and X_{c3} and the types of the saturation parameters to be evaluated are (1) $\Omega_{K_1}^{\infty}$ and $\Omega_{K_1, K_2}^{\infty}$ (if MCAL = 1, see equations (3.23)) or (2) $\Omega_{K_1}^{\infty}$, $\Omega_{K_1, K_2}^{\infty}$, Ω_{K_1} , Ω_{K_1, K_2} , $\chi_{K_1}^{MPAIR}$ and χ_{K_1, K_2}^{MPAIR} (if MCAL = 2, see equations (3.20a), equations (3.20b) and equations (3.23)). If MPUMP2 = 2 the X_{c3} type of combinations will not be considered and hence the corresponding saturation parameters will not be evaluated. NPARA is the number of the $L(j)$ parameters and NPAIR is the total number of the pairs 'rs' for which the calculations (if MCAL = 2) of $\chi^{MPAIR, s}$ are to be performed. MPAIR stands for any one of the NPAIR pairs.

After reading the above mentioned controlling and dimensioning data the program proceeds as follows:

- (i) If MCAL = 2, the various energy gaps ($E(J)$, $J = 1$, (NLEVEL-1)) are read alphanumerically as E12, E23, etc. These are used while giving the output of calculated XD's and XNR's.
- (ii) ($L(J)$, $J = 1$, NPARA), the various parameters characterizing the relaxations are read alphanumerically for example as 'a', 'b', 'c', etc.
- (iii) DO LOOP I = 1, KRELAX ; IRR(I), ($C(I, J)$, $J = 1$, NPARA), various relaxations (R's) and the coefficients $B(I, J)$'s for them (see equation (3.4)) are read and

stored in IRR and C respectively. The reason why they are not stored directly in IR and B will be clear a little later. The variable names IRR and IR for relaxations are used because the relaxations are read as fixed point variables e.g. $IRR(1) = R_{63} = 0603$, $IRR(7) = R_{21} = 0201$, etc.

- (iv) (IP(I), I = 1, NPUMP) various pumps (P's) are read as fixed point variables and stored in IP's e.g. $IP(1) = P_{25} = 0205$, $IP(4) = P_{13} = 0103$, etc.
- (v) (IPIR(I), I = 1, NPUMP), the characterizing indices for all the NPUMP pumps are read as IPIR's. $IPIR(I) = J$ implies that the I-th pump connects the same pair of levels as does the J-th relaxation. Any allowed combination will then not have both IP(I) and IR(J) in it because a combination having both these will not fulfill the rules of the 'inspection method'. Hence if $IPIR(I) = J$, while considering the combinations having I-th pump and certain relaxations one should exclude the J-th relaxation from the total of the relaxations.
- (vi) If MCAL = 2, the χ 's are also to be calculated and so 'r' (IPAIR) and 's' (JPAIR) for all the NPAIR pairs 'r' are read as (IPAIR(MPAIR), JPAIR(MPAIR), MPAIR = 1, NPAIR). These form a part of common storage area and are used in the subroutine 'ALGEBR' for the evaluation of XNR's (see equations (3.20b)).

After reading as above it prints the heading with NLEVEL, the number of the levels in the systems it is going to analyse and then reads and prints the corresponding energy level diagram. This completes the input.

The program now starts the evaluation of the various desired polynomial coefficients (if MCAL = 1, BETA's and if MCAL = 2, XD's, XNR's and BETA's) by considering the appropriate type of combinations e.g., X_{c2} , X_{c3} , etc. in that order. Note that the two limits of the types of the combinations is not written. These two limits depend upon the values of MPUMP1 and MPUMP2. However, usually MPUMP1 = 1 so that the polynomial coefficients obtained by considering X_{c1} type of combination are the ones evaluated first. These give us the denominators of the saturation parameters. The DO LOOP KPUMP = MPUMP1, MPUMP2 considers various types of combinations one by one. After getting a value of KPUMP here, MPUMP is set equal to (KPUMP-1). MPUMP is the number of the pumps present in each combination and it thus decides the type of the combinations to be considered presently. MPUMP is printed out and then MRELAX, the number of the relaxation to be present in each combination, is set equal to (NLEVEL-MPUMP-1). NRELAX, the total number of relaxations (IR's) is then set equal to (NRELAX-MPUMP) because certain MPUMP relaxations are to be ignored while preparing the set of IR's from that of IRR's for the present calculations. The values of MRELAX fix the order i.e. the sum of the powers of various L(J)'s in all the terms of the polynomials which are going to be evaluated while the number of the terms (MTERM) in the polynomials depends both on MRELAX and NPARA. Hence each time in the DO LOOP KPUMP = MPUMP1, MPUMP2 one evaluates for all MTERM

terms of the polynomials, the powers of all $L(J)$'s as $((LP(NTERM, J), NTERM = 1, MTERM), J = 1, NPARA)$. LP 's constitute a part of the common storage area and are used in the subroutine 'ALGEBR' in storing the contributions of each allowed combination in various terms of the polynomials. The LP 's are printed out to give us the information of the probable terms in the polynomials which are going to be evaluated (for the value of $MPUMP$ set earlier).

At this stage the program takes all possible sets of $MPUMP$ pumps from the read list of pumps (IP 's) one by one, each time thus fixing the category of the combinations to be considered and the specific polynomials coefficients to be evaluated, e.g. if $MPUMP = 2$ and we have taken the two pumps as $IP(1)$ and $IP(4)$ the combinations to be considered are $X_{c3(1,4)}$ (i.e. those having the first and the fourth pump) and the polynomial coefficients to be evaluated are (i) $BETA^{c3(1,4)}_s$, if $MCAL = 1$ (ii) $XD^{c3(1,4)}_s$, $XNR^{c3(1,4)}_s$ and $BETA^{c3(1,4)}_s$, if $MCAL = 2$. Now for this example, we know that we have to ignore the $IPIR(1)$ -th and $IPIR(4)$ -th relaxations (IRR 's). The various $IPIR$ values of the pumps taken are stored in a single dimensioned variable IQP which is then used for excluding the respective $MPUMP$ relaxations from the 'KRELAX' read relaxations (IRR 's) and putting the rest (i.e. $NRELAX$) of them in IR 's, the set of relaxations for the present calculations. The C 's corresponding to the IRR 's retained and set in IR 's are put in B 's. B 's form a part of the common storage area and are used in the subroutine 'ALGEBR' for the evaluation of $ALPHA$'s (see equations (3.8)) for the various allowed combinations. Before going to consider all the

combinations of the above fixed category for the evaluation of proper polynomial coefficients we initialize these to zero. After this we also initialize NGOOD, the number of allowed combinations and NBAD, the number of disallowed combinations of this category to zero. Now with this fixed set of MPUMP pumps, all possible sets of MRELAX relaxations (IR's) are taken one by one. The set of MPUMP pumps and a set of MRELAX relaxations together constitute a combination of the above fixed category. Now one has to test whether this combination is allowed or not. If it is allowed, further computations are to be done, otherwise the next combination is to be considered leaving this disallowed combination. For this purpose the MPUMP pumps and the MRELAX relaxations occurring in the combination under consideration are stored in a dimensioned variable IQ, which forms a part of the common storage area and is used in the subroutine 'SELECT' to test whether the combination is allowed or not. Various indices (I's) of the MRELAX relaxations (IR(I)'s) taken in the set are stored in a dimensioned variable IQR, which also forms a part of the common storage area, and will be used in the evaluation of ALPHA's (see equations (3.8)) corresponding to the combination, provided this is an allowed combination. The program now calls the subroutine 'SELECT'. If it turns out that this combination is disallowed, NBAD is increased by unity and the next combination is taken by taking the next set of MRELAX relaxations. On the otherhand if the combination is allowed, NGOOD is increased by unity before going to do the further calculations of the contributions of this combination to the proper polynomial coefficients. Note that the evaluation of the contributions to proper BETA's requires the evaluation of ALPHA's only (see equations (3.23)) while the

evaluation of the contributions to the proper XD's and XNR's requires the evaluation of $\Lambda(I,J)$'s also (see equations (3.20a) and equations (3.20b)). Hence if MCAL = 2, and the combination is found to be an allowed one the program initializes the $\Lambda(I,J)$'s to zero and calls the subroutine 'ILAAIJ', which gives a fresh matrix $\Lambda(I,J)$ corresponding to the allowed combination. $\Lambda(I,J)$'s form a part of the common storage area and are used in the subroutine 'ALGEBR' for the evaluation of the contributions to the XD's and XNR's. After evaluating $\Lambda(I,J)$'s in the subroutine 'ILAAIJ' one comes back to the main program 'SAT' and calls the subroutine 'ALGEBR' which actually performs the algebraic calculations for the appropriate ALPHA's and then evaluates and stores the contributions to the proper polynomial coefficients. Had MCAL been equal to unity, the program would have skipped the calling of the subroutine 'ILAAIJ' and would have directly called the subroutine 'ALGEBR' for evaluating and storing of the contributions to BETA's. After returning from the subroutine 'ALGEBR' the program takes the next combination of this category by taking next set of MRELAX relaxations and goes through the same process as explained above. When all the combinations of this category are exhausted we get the corresponding polynomial coefficients (particular BETA's if MCAL = 1 or if MCAL = 2, XD's and XNR's also), which are calculated in the subroutine 'ALGEBR'. BETA's, XD's and XNR's form a part of the common storage area. These are printed out in the main program. Afterwards, the program goes back and takes the next set of MPUMP pumps and proceeds to do the respective calculations and print the results in the manner similar to that explained above for the new set. On exhausting all possible sets of MPUMP pumps, the program goes still back to take the next value of MPUMP

which is actually greater by unity than the earlier MPUMP value, for which all the calculations have been done. Again all possible categories of this type of combinations (having MPUMP pumps) are considered one by one and the calculations are done in the manner just similar to that adopted earlier. When MPUMP equals (MPUMP2-1) the program comes back to take the next system. Finally, when all the systems are finished the program stops.

The Subroutine 'SELECT'

This subroutine is based on the inspection rules¹ and is used to test whether a particular combination is allowed or not. A parameter 'LOOP' is used for this purpose. Before calling this subroutine we set LOOP = 0 in the main program and if during the test in the subroutine 'SELECT' the combination is found to be disallowed the LOOP is set equal to unity. Actually all pumps and the relaxations occurring in the combination in question are taken in this subroutine through the IQ's from the common storage area. Each of these IQ's is here split into ISUB and JSUB which give us the two levels connected by it. Finally, these ISUB's and JSUB's are used to test whether the combination is allowed or not and resetting LOOP = 1 in the latter case. The ISUB's and JSUB's form a part of the common storage area and are also used (if MCAL = 2) for the evaluation of A(I,J)'s for the combination (in case it is an allowed combination) in the subroutine 'ILAALJ'. One goes back to the main program with the value of LOOP which is same as zero in case the combination is allowed and is reset to unity if the combination is disallowed.

The Subroutine 'ILAAIJ'

This subroutine is called if (i) $MCAL = 2$ and (ii) the combination is allowed. If $MCAL = 1$ it is not needed to calculate $A(I,J)$'s for the allowed combination. Based on the inspection method¹ this subroutine uses $ISUB$'s and $JSUB$'s of the allowed combination calculated in the subroutine 'SELECT' and first finds out the "intermediate levels"¹ for it. It then calculates $A(1,J)$, $J = 1, NLEVEL$. It also sets, according to equation (3.14) ($A(I,1)$, $I = 1, NLEVEL$) all equal to unity. Using the calculated $A(1,J)$'s and $A(I,1)$'s and the $ISUB$'s and $JSUB$'s, the rest of $A(I,J)$'s are also calculated. Finally, it calculates $A(\beta+1,J)$, $J = 1, NLEVEL$ using the equation (3.17) and goes back to the main program.

The Subroutine 'ALGEBR'

As has been mentioned earlier this subroutine calculates the contributions from the allowed combination to the proper polynomial coefficients and stores them in the variable $BETA$'s (if $MCAL = 1$) or in the variables $BETA$'s, XD 's and XNR 's (if $MCAL = 2$). Here, it first calculates $ALPHA$'s (see equations (3.8)) for which it takes IQR 's from the common storage area and back-calculates the indices (I 's) of the $MRELAX$ relaxations ($IR(I)$'s) occurring in the combination. Again it takes from the common storage area the B 's corresponding to these relaxations (indices I 's) and calculates one by one the coefficients of all possible $(NPARA)^{(MRELAX)}$ pseudo-terms (some of which may correspond to one of the terms of the $MTERM$ terms) encountered while making the product of $MRELAX$ relaxations from the first principles; for example, if one multiplies

$(x+y+z)$ by $(x+y+z)$ one gets nine pseudo-terms, whereas actually there are six terms ($MTERM = 6$). So, each time while evaluating a pseudo-term coefficient it evaluates the powers of the various $L(J)$ parameters occurring in this term as $(LLP(J), J = 1, NPARA)$ and compares them with $MTERM$ sets $((LP(NTERM, J), J = 1, NPARA), NTERM = 1, MTERM)$ which are already stored in a part of the common storage area. The moment it finds that for a particular $NTERM$ value $(LP(NTERM, J) = LLP(J), J = 1, NPARA)$ it puts the corresponding term coefficient calculated in the appropriate $ALPHA$ (which corresponds to the particular $NTERM$ value). After evaluating the $ALPHA$'s in this manner, the contributions of this combination to the appropriate polynomial coefficients are calculated and stored. While calculating contributions to XD 's and XNR 's, $A(I, J)$'s obtained earlier in the subroutine 'ILAAIJ' are taken from the common storage area. Also the values of $NPAIR$ r's and s's ($IPAIR$'s and $JPAIR$'s) required for the calculation of the contributions to XNR 's are taken from the common storage area. From here we return to the main program and proceed as explained under the main program 'SAT'.

The IBM 7044 computer FORTRAN program is given in the Appendix. A sample data and the corresponding output have also been given in this Appendix.

III.4 EXAMPLES

As examples of our calculations we have considered a six-level and a ten-level system both of which are electron-nuclear coupled systems. In these examples the relaxation mechanisms are supposed to be those of the type discussed by Stephen and Fraenkel^{2,3} for the dilute solutions of

free radicals (see also Chapter II). Hence, we can write the various relaxation R's (see equation (3.4)) as linear combination of three parameters (NPARA = 3), $L(1) = a$, $L(2) = b$ and $L(3) = c$. Here, according to Stephen and Fraenkel^{2,3}, 'a' represents intramolecular dipole-dipole interaction, 'b' represents a cross term between this and the g-tensor anisotropy and 'c' represents the total sum of all other effects which cause the electron flip without involving the nuclei.

It is clear from the sets of equations (3.19a), (3.19b), (3.20a) and (3.20b) that in 'the finite-temperature case with linear approximation', the saturation parameters are quotients of polynomials of various degrees in the relaxation parameters 'a', 'b' and 'c', the coefficients of the terms of these polynomials being, in general, linear combinations of the energy gaps of the system. On the otherhand, in 'the infinitely high-temperature case' (see sets of equations (3.22) and (3.23)), the saturation parameters, Ω^∞ 's are again quotients of polynomials of various degrees in 'a', 'b' and 'c' but here unlike 'the case of finite-temperature with linear approximation' the coefficient of the terms of the polynomials are numerical constants. χ 's, however, are not defined in 'the infinite-temperature case'.

For a particular system the denominators of all Ω 's are the same and the denominators of all χ 's corresponding to the same MPAIR are also same. The numerators for the various saturation parameters are different. As will be seen later, both in the six-level and the ten-level systems taken here, each relaxation is actually not a linear combination of all the three relaxation parameters 'a', 'b' and 'c' and hence in the various polynomials all the respective MTERM terms do not actually exist.

While giving the results we shall omit the listing of the non-existing terms of the polynomials. Results will be given in tabular form. For 'the finite-temperature case with linear approximation' each table represents a polynomial (a numerator or a denominator of a saturation parameter), whereas for 'the infinite-temperature case' the tables sometimes give more than one polynomial. In the latter case each term in the polynomials is given in units of $(1/6)^p$ where p represents the order of the polynomial. This is done so as to enable ourselves to compare the present calculations for 'the infinitely high-temperature case' with those of Stephen and Fraenkel, who have used such units in their earlier work on the calculations of $\Omega_{K_1}^\infty$'s.

We shall now describe the two examples and give the results.

The Six-Level System

This is an electron-nuclear coupled system (NLEVEL = 6) with nuclear spin $I = 1$ and electron spin $S = \frac{1}{2}$ (see Fig. III.1). There are eleven relaxations (KRELAX = 11) present in this system and in the extreme motional narrowing case, these are^{2,3} as given below:

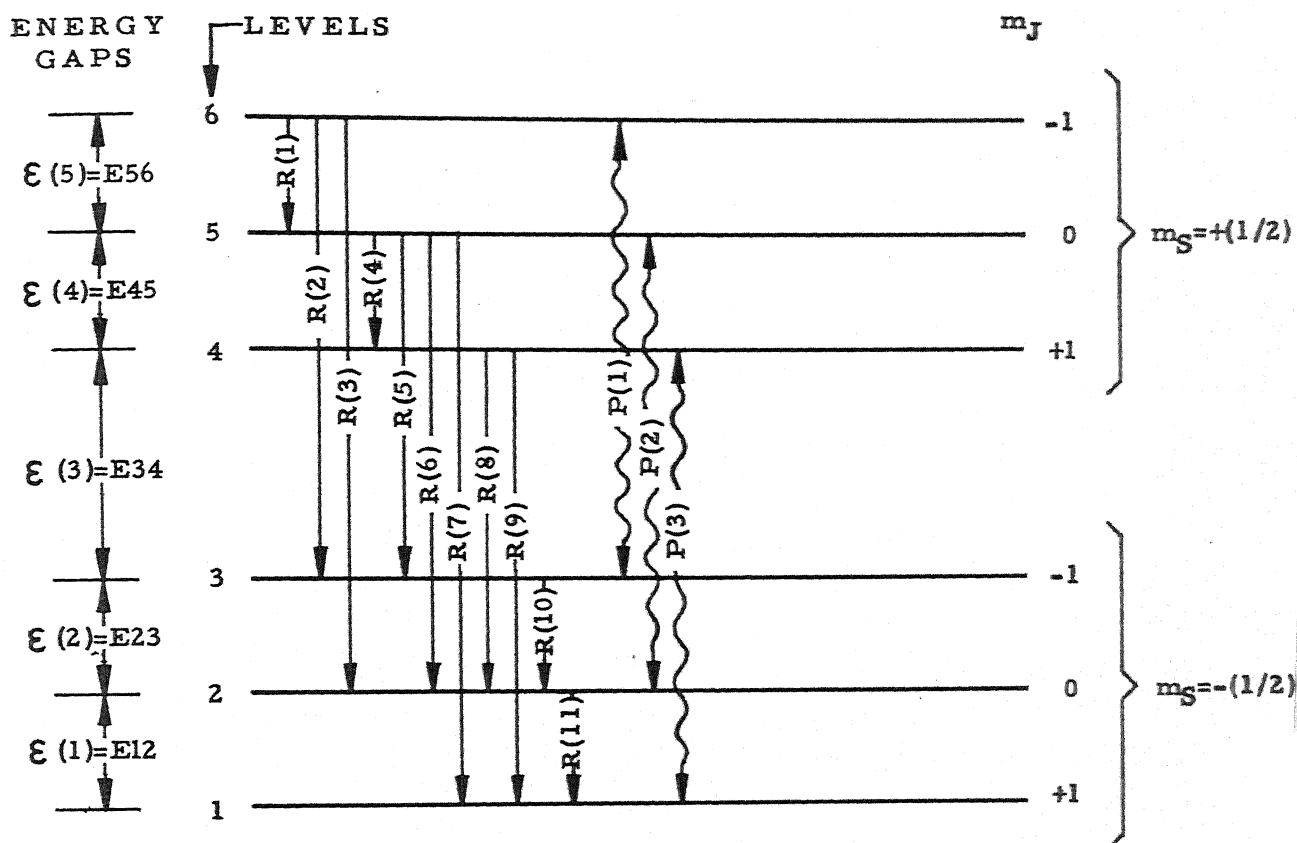


FIG. III. 1 ENERGY LEVELS FOR THE SPIN SYSTEM WITH ($S = 1/2$ and $I = 1$). ENERGY LEVELS ARE LABELED BY m_S, m_J VALUES. THE POSSIBLE RELAXATIONS FOR EXTREME MOTIONAL NARROWING ARE SHOWN. THE SYSTEM CONTAINS THREE RADIATIVE INDUCED TRANSITIONS i.e. PUMPS WHICH ARE ALSO SHOWN HERE.

$$\begin{aligned}
R(1) &= R_{65} = 0605 = \frac{1}{2}a \\
R(2) &= R_{63} = 0603 = a-b+c \\
R(3) &= R_{62} = 0602 = \frac{1}{2}a \\
R(4) &= R_{54} = 0504 = \frac{1}{2}a \\
R(5) &= R_{53} = 0503 = 2a \\
R(6) &= R_{52} = 0502 = c \\
R(7) &= R_{51} = 0501 = \frac{1}{2}a \\
R(8) &= R_{42} = 0402 = 2a \\
R(9) &= R_{41} = 0401 = a+b+c \\
R(10) &= R_{32} = 0302 = \frac{1}{2}a \\
R(11) &= R_{21} = 0201 = \frac{1}{2}a
\end{aligned}
\tag{3.24}$$

As is indicated in the Fig. III.1 we take in this example three pumps (NPUMP = $t = 3$) which are

$$\begin{aligned}
P(1) &= P_{p_1 q_1} = P_{36} = 0306 \\
P(2) &= P_{p_2 q_2} = P_{25} = 0205 \\
P(3) &= P_{p_3 q_3} = P_{14} = 0104
\end{aligned}
\tag{3.25}$$

For each of the 'NPAIR' pairs 'r and s' the saturation factor is defined by equation (3.1), so that the MPAIR-th saturation factor Z_{MPAIR} is given by

$$\begin{aligned}
& 1 + \sum_{K_1=1}^3 P(K_1) \chi_{K_1}^{\text{MPAIR}} + \sum_{K_1 > K_2=1}^3 P(K_1) P(K_2) \chi_{K_1, K_2}^{\text{MPAIR}} \\
& + \sum_{K_1 > K_2 > K_3=1}^3 P(K_1) P(K_2) P(K_3) \chi_{K_1, K_2, K_3}^{\text{MPAIR}} \\
Z_{\text{MPAIR}} = & \frac{\quad}{1 + \sum_{K_1=1}^3 P(K_1) \Omega_{K_1} + \sum_{K_1 > K_2=1}^3 P(K_1) P(K_2) \Omega_{K_1, K_2} \\
& + \sum_{K_1 > K_2 > K_3=1}^3 P(K_1) P(K_2) P(K_3) \Omega_{K_1, K_2, K_3}} \quad (3.26)
\end{aligned}$$

If we take $\text{NPAIR} = 3$ and the three 'rs' pairs as (06,03), (05,02) and (04,01), the various saturation parameters χ 's and Ω 's are $\chi_2^1, \chi_3^1, \chi_1^2, \chi_3^2, \chi_1^3, \chi_2^3, \chi_{3,2}^1, \chi_{3,1}^2, \chi_{2,1}^3$, (the rest of χ 's are zero) and $\Omega_1, \Omega_2, \Omega_3, \Omega_{3,2}, \Omega_{3,1}, \Omega_{2,1}, \Omega_{3,2,1}$. The denominators of all these are fifth degree polynomials in 'a', 'b' and 'c'. The numerators for $\Omega_1, \Omega_2, \Omega_3, \chi_2^1, \chi_3^1, \chi_1^2, \chi_3^2, \chi_1^3$, and χ_2^3 are fourth degree polynomials; those of $\Omega_{3,2}, \Omega_{3,1}, \Omega_{2,1}, \chi_{3,2}^1, \chi_{3,1}^2$ and $\chi_{2,1}^3$ are third degree polynomials and those for $\Omega_{3,2,1}$ are second degree polynomials in 'a', 'b' and 'c'.

Since space does not permit us to give the complete results of the calculation, we shall restrict ourselves to a few illustrative results. In Tables III.1 to III.4 are thus given the results of our calculations on $\Omega_{3,2}$ and χ_3^2 for the finite-temperature case with the linear approximation. We have also given in Tables III.5 and III.6 the results of our calculation on $\Omega_{K_1}^\infty$'s in this system and the results of Stephen and Fraenkel^{2,3} are also compared.

TABLE III.1

Common Denominator of all Ω 's in the Six-Level System

MTERM = 21

XD^{c1}(MTERM, J), obtained by summing over the allowed combinations of the type and category X_{c1}. See sets of equations (3.19a) and (3.20a). Number of allowed combinations = 192. Number of disallowed combinations = 270.

MTERM	$\prod_{i=1}^3 \left\{ L(i) \right\}$ LP(MTERM, i)	J=1					J=2					J=3					J=4					J=5					J=6				
		Coeff. of					Coeff. of					Coeff. of					Coeff. of					Coeff. of					Coeff. of				
		$\sum(0)/kT$					$\sum(1)/kT$					$\sum(2)/kT$					$\sum(3)/kT$					$\sum(4)/kT$					$\sum(5)/kT$				
1	a^5	2.1667x10 ²					-1.8056x10 ²					-2.8278x10 ²					-3.7458x10 ²					-2.5535x10 ²					-1.0694x10 ²				
2	$a^4 b$	-1.0394x10 ⁻⁶					1.0747x10 ⁻⁶					-2.5000x10 ¹					-2.0833x10 ¹					2.1875x10 ¹					1.3542x10 ¹				
3	$a^4 c$	4.4479x10 ²					-3.7066x10 ²					-6.1236x10 ²					-8.4781x10 ²					-5.7680x10 ²					-2.0226x10 ²				
4	$a^3 b^2$	-8.3333x10 ¹					-6.9444x10 ¹					1.2431x10 ²					1.6250x10 ²					9.0278x10 ¹					4.9306x10 ¹				
5	$a^3 bc$	-5.2899x10 ⁻⁷					1.8254x10 ⁻⁷					-1.8750x10 ¹					-1.6667x10 ¹					1.6667x10 ¹					1.0417x10 ¹				
6	$a^3 c^2$	3.0000x10 ²					-2.5000x10 ²					-4.3417x10 ²					-6.1833x10 ²					-4.1333x10 ²					-1.2917x10 ²				
8	$a^2 b^2 c$	-6.6667x10 ¹					5.5556x10 ¹					1.0111x10 ²					1.4667x10 ²					9.5556x10 ¹					2.7778x10 ¹				
10	$a^2 c^3$	6.6667x10 ¹					-5.5556x10 ¹					-1.0111x10 ²					-1.4667x10 ²					-9.5556x10 ¹					-2.7778x10 ¹				

TABLE III.2

Numerator of $\Omega_{3,2}$ in the Six-Level System

MTERM = 10

NTERM	$\prod_{i=1}^3 \left\{ L(i) \right\}$	LP(NTERM, i)	XD c3(3,2) (NTERM, J), obtained by summing over the allowed combinations of the type and category Xc3(3,2). See sets of equations (3.19a) and (3.20a). Number of allowed combinations = 52. Number of disallowed combinations = 52.					
			J=1 Coeff. of $\zeta(0)/kT$	J=2 Coeff. of $\zeta(1)/kT$	J=3 Coeff. of $\zeta(2)/kT$	J=4 Coeff. of $\zeta(3)/kT$	J=5 Coeff. of $\zeta(4)/kT$	J=6 Coeff. of $\zeta(5)/kT$
1	3_a		1.0833×10^2	-9.0278×10^1	-9.0694×10^1	-1.2861×10^2	-7.8889×10^1	-9.0278×10^0
2	$2_a b$		6.6667×10^1	-5.5556×10^1	-6.7778×10^1	-9.1111×10^1	-4.0000×10^1	-5.5556×10^0
3	$2_a c$		6.6667×10^1	-5.5556×10^1	-6.7778×10^1	-9.1111×10^1	-4.0000×10^1	-5.5556×10^0

TABLE III.3

Common Denominator of all χ^2 's in the Six-Level System

MTERM = 21

NTERM	$\prod_{i=1}^3 \prod \left\{ L(i) \right\}$ LP(NTERM, i)	XNR ^{cl} (NTERM, J, 2), obtained by summing over the allowed combinations of the type and category X _{cl} . See sets of equations (3.19b) and (3.20b). Number of allowed combinations = 192. Number of disallowed combinations = 270.					
		J=1 Coeff. of $\sum(0)/kT$	J=2 Coeff. of $\sum(1)/kT$	J=3 Coeff. of $\sum(2)/kT$	J=4 Coeff. of $\sum(3)/kT$	J=5 Coeff. of $\sum(4)/kT$	J=6 Coeff. of $\sum(5)/kT$
1	a^5	0.0	0.0	3.6111×10^1	3.6111×10^1	3.6111×10^1	0.0
2	a^4_b	0.0	0.0	-1.2107×10^{-7}	-1.2107×10^{-7}	-1.2107×10^{-7}	0.0
3	a^4_c	0.0	0.0	7.4132×10^1	7.4132×10^1	7.4132×10^1	0.0
4	$a^3_{b^2}$	0.0	0.0	-1.3889×10^1	-1.3889×10^1	-1.3889×10^1	0.0
5	a^3_{bc}	0.0	0.0	-5.2154×10^{-8}	-5.2154×10^{-8}	-5.2154×10^{-8}	0.0
6	a^3_c	0.0	0.0	5.0000×10^1	5.0000×10^1	5.0000×10^1	0.0
8	$a^2_{b^2c}$	0.0	0.0	-1.1111×10^1	-1.1111×10^1	-1.1111×10^1	0.0
10	$a^2_{c^3}$	0.0	0.0	1.1111×10^1	1.1111×10^1	1.1111×10^1	0.0

TABLE III.4

Numerator of χ_3^2 in the Six-Level System

MTERM = 15

NTERM	$\prod_{i=1}^3 \{L(i)\}$	LP(NTERM, i)	XNR ^{c2(3)} (NTERM, J, 2), obtained by summing over the allowed combinations of the type and category Xc2(3). See sets of equations (3.19b) and (3.20b). Number of allowed combinations = 96. Number of disallowed combinations = 114.					
			J=1 Coeff. of $\zeta(0)/kT$	J=2 Coeff. of $\zeta(1)/kT$	J=3 Coeff. of $\zeta(2)/kT$	J=4 Coeff. of $\zeta(3)/kT$	J=5 Coeff. of $\zeta(4)/kT$	J=6 Coeff. of $\zeta(5)/kT$
1	a^4		0.0	2.2569×10^0	2.4653×10^1	2.4653×10^1	2.2396×10^1	0.0
2	$a^3 b$		0.0	-1.3889×10^0	-1.5278×10^1	-1.5278×10^1	-1.3889×10^1	0.0
3	$a^3 c$		0.0	1.3889×10^0	3.3333×10^1	3.3333×10^1	3.1944×10^1	0.0
5	$a^2 bc$		0.0	0.0	-1.1111×10^1	-1.1111×10^1	-1.1111×10^1	0.0
6	$a^2 c^2$		0.0	0.0	1.1111×10^1	1.1111×10^1	1.1111×10^1	0.0

TABLE III.5

Common Denominator for all Ω^∞ 's in the Six-Level System

MTERM= 21

BETA ^{cl} (MTERM), obtained by summing over the allowed combinations of the type and category X _{cl} . See sets of equations (3.22) and (3.23). Number of allowed combinations = 192. Number of disallowed combinations = 270.			
MTERM	$\prod_{i=1}^3 \left\{ L(i) \right\}$ LP(MTERM,i)	Present Calculations	S-F (*) Calculations
1	a^5	280799.71	280800.00
2	$a^4 b$	-156909.23x10 ⁻⁹	-
3	$a^4 c$	96074.91	96075.00
4	$a^3 b^2$	-2999.99	-
5	$a^3 bc$	-112652.78x10 ⁻¹⁰	-
6	$a^3 c^2$	10799.99	10800.00
8	$a^2 b^2 c$	-399.99	-
10	$a^2 c$	399.99	400.00

(*) Stephen and Fraenkel (see ref. 2 and 3). These authors were interested mainly in the ratios of the various Ω^∞ 's and hence the common denominator was not of interest to them. Therefore, for simplicity these workers assumed $b =$ and hence their polynomial does not contain terms involving b . However, if one is interested in the calculation of individual saturation parameters the assumption that $b = 0$ cannot be made.

TABLE III.6

Numerator for $\Omega_{K_1}^{\infty}$'s ($K_1=1,2,3$) in the Six-Level System

MTERM = 15

BETA $c_2(K_1)$ (MTERM), obtained by summing over the allowed combinations of the type and category $X_{c_2(K_1)}$. See sets of equations (3.22) and (3.23).

MTERM	$\prod_{i=1}^3 \{L(i)\}$ LP(MTERM, i)	$K_1 = 1$			$K_1 = 2$			$K_1 = 3$		
		Number of Combinations			Number of Combinations			Number of Combinations		
		1- Allowed = 96	2- Disallowed = 114	Present	1- Allowed = 64	2- Disallowed = 146	Present	1- Allowed = 96	2- Disallowed = 114	Present
		Calculations	S-F (*)	Calculations	Calculations	S-F (*)	Calculations	Calculations	S-F (*)	Calculations
1	a^4	29024.98	29025.00	38025.98	38025.00	29024.98	29025.00	29025.00		29025.00
2	$a^3 b$	2999.99	3000.00	-11265.3x10 ⁻⁹	0.00	-2999.99	-3000.00			
3	$a^3 c$	6899.99	6900.00	7799.99	7800.00	6899.99	6900.00			
4	$a^2 b^2$	0.00	0.00	-399.99	-400.00	0.00	0.00			
5	$a^2 bc$	399.99	400.00	0.00	0.00	-399.99	-400.00			
6	$a^2 c^2$	399.99	400.00	399.99	400.00	399.99	400.00			

(*) Stephen and Fraenkel (see ref. 2 and ref.3).

The Ten-Level System

This is also an electron-nuclear coupled system (NLEVEL=10) with four equivalent protons ($I=\frac{1}{2}$) and one odd electron ($S=\frac{1}{2}$). There are twentyor relaxations (KRELAX=21) present in it and according to Stephen and Fraenkel², in the extreme motional narrowing case these are given by

$$\begin{aligned} R(1) &= R_{1009} = 1009 = a \\ R(2) &= R_{1005} = 1005 = 4a-2b+c \\ R(3) &= R_{1004} = 1004 = \frac{2}{3}a \\ R(4) &= R_{98} = 0908 = 3a \\ R(5) &= R_{95} = 0905 = 4a \\ R(6) &= R_{94} = 0904 = 4a-4b+4c \\ R(7) &= R_{93} = 0903 = 2a \\ R(8) &= R_{87} = 0807 = 3a \\ R(9) &= R_{84} = 0804 = 12a \\ R(10) &= R_{83} = 0803 = 6c \\ R(11) &= R_{82} = 0802 = 2a \\ R(12) &= R_{76} = 0706 = a \\ R(13) &= R_{73} = 0703 = 12a \\ R(14) &= R_{72} = 0702 = 4a+4b+4c \\ R(15) &= R_{71} = 0701 = \frac{2}{3}a \\ R(16) &= R_{62} = 0602 = 4a \\ R(17) &= R_{61} = 0601 = 4a+2b+c \\ R(18) &= R_{54} = 0504 = a \\ R(19) &= R_{43} = 0403 = 3a \\ R(20) &= R_{32} = 0302 = 3a \\ R(21) &= R_{21} = 0201 = a \end{aligned}$$

(3.27)

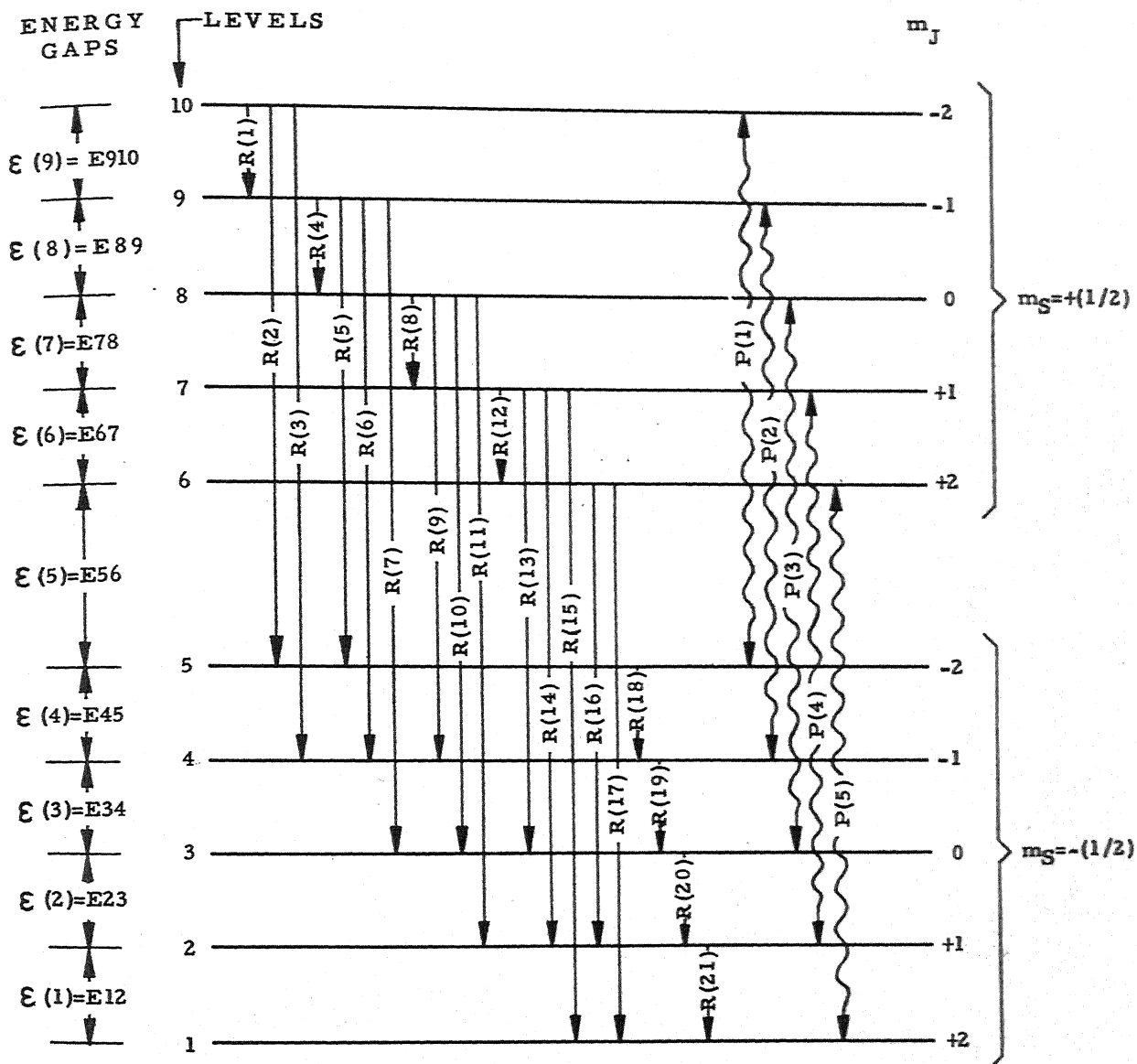


FIG. III. 2 ENERGY LEVELS DIAGRAM FOR SPIN SYSTEM WITH FOUR EQUIVALENT PROTONS ($I = 1/2$) AND ONE ELECTRON ($S = 1/2$). ENERGY LEVELS ARE LABELED BY m_S , m_J VALUES. THE POSSIBLE RELAXATIONS FOR EXTREME MOTIONAL NARROWING ARE SHOWN. THE SYSTEM CONTAINS FIVE RADIATIVE INDUCED TRANSITIONS i.e. PUMPS. THESE ARE ALSO SHOWN HERE.

In this example only five pumps are supposed to be present (NPUMP = 5 = t). They are

$$\begin{aligned}
 P(1) &= P_{p_1 q_1} = P_{0510} = 0510 \\
 P(2) &= P_{p_2 q_2} \quad P_{0409} = 0409 \\
 P(3) &= P_{p_3 q_3} \quad P_{0308} = 0308 \\
 P(4) &= P_{p_4 q_4} \quad P_{0207} = 0207 \\
 P(5) &= P_{p_5 q_5} \quad P_{0106} = 0106
 \end{aligned} \tag{3.28}$$

The MPAIR-th saturation factor Z_{MPAIR} is again defined by an equation similar to equation (3.26). However, in this example we shall be giving the results of our calculations of $\Omega_{K_1}^{\infty}$'s ($K_1 = 1, 2, \dots, 5$). Table III.7 gives the common denominator of all these and Tables III.8 to III.12 give the various numerators. We have compared our results with those of Stephen and Fraenkel^{2,3} in these tables also.

It may be pointed out here that the 'relaxation cofactors' defined by these authors are simply the various terms of the polynomials in our formalism. All our common calculations agree exactly except for the fact that some of the nonzero terms of the polynomials are missing from the tables of Relaxation Cofactors given by these workers. However we have noticed that these terms are much smaller as compared with the other terms of the corresponding polynomials.

We are not aware of any other attempts in the literature made so far for the evaluation of $\Omega_{K_1, K_2}^{\infty}$'s, $\Omega_{K_1, K_2, K_3}^{\infty}$'s, etc. and for the saturation parameters at finite temperature with the linear approximation.

TABLE III.7

Common Denominator of all Ω^∞ 's in the Ten-Level System

MTERM = 55

NTERM	$\prod_{i=1}^3 \{L(i)\}^{LP(NTERM,i)}$	BETA ^{c1} (NTERM) $\times 10^{-8}$, obtained by summing over the allowed combinations of the type and category X _{c1} . See sets of equations (3.22) and (3.23). Number of allowed combinations = 27648. Number of disallowed combinations = 266282.	
		Present Calculations	S-F (*) Calculations
1	a^9	294201.40×10^2	294202.00×10^2
2	$a^8 b$	-31.00×10^{-2}	-
3	$a^8 c$	102610.51×10^2	102610.50×10^2
4	$a^7 b^2$	-283891.16×10^0	-
5	$a^7 bc$	9.00×10^{-2}	-
6	$a^7 c^2$	131937.54×10^1	131937.60×10^1
7	$a^6 b^3$	-6.40×10^{-2}	-
8	$a^6 b^2 c$	$-663384.75 \times 10^{-1}$	-
9	$a^6 bc^2$	8.00×10^{-3}	-
10	$a^6 c^3$	7846.92×10^1	7846.90×10^1
11	$a^5 b^4$	663.55×10^0	-
12	$a^5 b^3 c$	-5.32×10^{-3}	-
13	$a^5 b^2 c^2$	-4611.68×10^0	-
14	$a^5 bc^3$	2.30×10^{-4}	-
15	$a^5 c^4$	215.65×10^1	215.65×10^1
17	$a^4 b^4 c$	88.47×10^0	-
19	$a^4 b^2 c^3$	-110.59×10^0	-
21	$a^4 c^5$	2211.84×10^{-2}	2211.84×10^{-2}

(*) Stephen and Fraenkel (ref.2 and ref.3) were interested mainly in the ratios of the various Ω^∞ 's and hence the common denominator was not of interest to them. Therefore, for simplicity these workers set $b=0$ and hence their polynomial does not contain terms involving b . However, for calculation of individual Ω^∞ 's one cannot set $b=0$.

TABLE III.8

Numerator for Ω_1^∞ in the Ten-Level System

MTERM = 45

NTERM	$\prod_{i=1}^3 \{L(i)\}^{LP(NTERM,i)}$	BETA ^{c2(1)} (NTERM) $\times 10^{-8}$, obtained by summing over the allowed combinations of the type and category $X_{c2(1)}$. See sets of equations (3.22) and (3.23). Number of allowed combinations = 13824. Number of disallowed combinations = 112146.	
		Present Calculations	S-F (*) Calculations
1	a^8	935220.31	935221.00
2	$a^7 b$	59551.69	59552.00
3	$a^7 c$	296358.82	296359.00
4	$a^6 b^2$	-5225.44	-5225.50
5	$a^6 bc$	16957.90	12348.00
6	$a^6 c^2$	32497.45	32497.00
7	$a^5 b^3$	-331.78	-331.78
8	$a^5 b^2 c$	-862.62	-862.62
9	$a^5 bc^2$	1526.17	1526.20
10	$a^5 c^3$	1459.81	1459.80
12	$a^4 b^3 c$	-44.237	-44.237
13	$a^4 b^2 c^2$	-22.118	-44.237
14	$a^4 bc^3$	44.237	44.237
15	$a^4 c^4$	22.118	22.118

(*) Stephen and Fraenkel (ref. 2 and ref. 3). The discrepancy between our result and that of Stephen and Fraenkel in items "5" and "1" is presumably due to an error in the results of Stephen and Fraenkel.

TABLE III.9

Numerator for Ω_2^∞ in the Ten-Level System

MTERM = 45

NTERM	$\prod_{i=1}^3 \{L(i)\}^{LP(NTERM,i)}$	BETA ^{c2(2)} (NTERM) $\times 10^{-8}$, obtained by summing over the allowed combinations of the type and category X _{c2(2)} . See sets of equations (3.22) and (3.23). Number of allowed combinations = 9216. Number of disallowed combinations = 116754.	
		Present Calculations	S-F (*) Calculations
1	a^8	550168.58	550169.00
2	$a^7 b$	41196.99	41197.00
3	$a^7 c$	150078.29	150078.00
4	$a^6 b^2$	-2220.82	-2220.80
5	$a^6 bc$	8105.67	8105.70
6	$a^6 c^2$	13354.50	13355.00
7	$a^5 b^3$	-165.89	-165.89
8	$a^5 b^2 c$	-464.49	-464.49
9	$a^5 bc^2$	389.84	389.84
10	$a^5 c^3$	464.49	464.49
12	$a^4 b^3 c$	-22.118	-22.118
13	$a^4 b^2 c^2$	-22.118	-22.118
14	$a^4 bc^3$	5.53	5.53
15	$a^4 c^4$	5.53	5.53

(*) Stephen and Fraenkel (ref. 2 and ref. 3)

TABLE III.10

Numerator for Ω_3^∞ in the Ten-Level System

MTERM = 45

NTERM	$\prod_{i=1}^3 \{L(i)\}^{LP(NTERM,i)}$	BETA ^{c2(3)} (NTERM)x10 ⁻⁸ , obtained by summing over the allowed combinations of the type and category X _{c2(3)} . See sets of equations (3.22) and (3.23). Number of allowed combinations = 9216. Number of disallowed combinations = 116754.	
		Present Calculations	S-F (*) Calculations
1	a ⁸	664875.34	664877.00
2	a ⁷ b	165144.64x10 ⁻⁶	0.00
3	a ⁷ c	140900.80	140901.00
4	a ⁶ b ²	-6353.47	-6353.50
5	a ⁶ bc	12712.05x10 ⁻⁶	0.00
6	a ⁶ c ²	10596.08	10596.00
7	a ⁵ b ³	-391.03x10 ⁻⁶	0.00
8	a ⁵ b ² c	-630.37	-630.37
9	a ⁵ bc ²	2349.00x10 ⁻⁷	0.00
10	a ⁵ c ³	331.78	331.78
11	a ⁴ b ⁴	14.75	14.75
12	a ⁴ b ³ c	-3.00x10 ⁻⁸	0.00
13	a ⁴ b ² c ²	-18.432	-18.432
14	a ⁴ bc ³	2.00x10 ⁻⁸	0.00
15	a ⁴ c ⁴	3.686	3.686

(*) Stephen and Fraenkel (ref. 2 and ref. 3).

TABLE III.11

Numerator for Ω_4^∞ in the Ten-Level System

MTER = 45

$\text{NTERM} \prod_{i=1}^3 \{L(i)\}^{LP(\text{NTERM}, i)}$		$\text{BETA}^{c2(4)}(\text{NTERM}) \times 10^{-8}$, obtained by summing over the allowed combinations of the type and category $X_{c2(4)}$. See sets of equations (3.22) and (3.23). Number of allowed combinations = 9216. Number of disallowed combinations = 116754.	
		Present Calculations	S-F (*) Calculations
1	a^8	550168.58	550169.00
2	$a^7 b$	-41196.99	-41197.00
3	$a^7 c$	150078.29	150078.00
4	$a^6 b^2$	-2220.82	-2220.80
5	$a^6 bc$	-8105.62	-8105.70
6	$a^6 c^2$	13354.50	13355.00
7	$a^5 b^3$	165.89	165.89
8	$a^5 b^2 c$	-464.49	-464.49
9	$a^5 bc^2$	-389.84	-389.84
10	$a^5 c^3$	464.49	464.49
12	$a^4 b^3 c$	22.118	22.118
13	$a^4 b^2 c^2$	-22.118	-22.118
14	$a^4 bc^3$	-5.53	-5.53
15	$a^4 c^4$	5.53	5.53

(*) Stephen and Fraenkel (ref. 2 and ref. 3).

TABLE III.12

Numerator for Ω_5^∞ in the Ten-Level System

MTERM = 45

NTERM	$\prod_{i=1}^3 \{L(i)\}^{LP(NTERM,i)}$	BETA ^{c2(5)} (NTERM)x10 ⁻⁸ , obtained by summing over the allowed combinations of the type and category $X_{c2(5)}$. See sets of equations (3.22) and (3.23). Number of allowed combinations = 13824. Number of disallowed combinations = 112146.	
		Present Calculations	S-F (*) Calculations
1	a^8	935220.26	935221.00
2	$a^7 b$	-59550.87	-59552.00
3	$a^7 c$	296358.81	296359.00
4	$a^6 b^2$	-5225.56	-5225.50
5	$a^6 bc$	-16957.78	-12348.00
6	$a^6 c^2$	32497.45	32497.00
7	$a^5 b^3$	331.78	331.78
8	$a^5 b^2 c$	-862.62	-862.62
9	$a^5 bc^2$	-1526.17	-1526.20
10	$a^5 c^3$	1459.81	1459.80
12	$a^4 b^3 c$	44.237	44.237
13	$a^4 b^2 c^2$	-22.118	-44.237
14	$a^4 bc^3$	-44.237	-44.237
15	$a^4 c^4$	22.118	22.118

(*) Stephen and Fraenkel (ref. 2 and ref. 3). The discrepancy between our result and that of Stephen and Fraenkel in items "5" and "13" is presumably due to an error in the results of Stephen and Fraenkel.

III.5 CONCLUSION

The present formalism for the evaluation of saturation parameters has been found to be satisfactory for the computer programming of the otherwise rather tedious calculations. The procedure adopted here yields valuable results on the saturation behaviour of multilevel-multiresonance systems without the necessity of involving the high temperature approximation. Since there are many systems (typical one being the electron-nuclear coupled system) where this procedure can be adopted it is hoped that investigation of the relaxation processes in such systems will be helped considerably by the analysis and use of computer programs such as the one outlined here.

The IBM 7044 computer FORTRAN program written for the calculations of the various saturation parameters is given in the Appendix. A sample data and the corresponding output have also been given.

REFERENCES

1. J.D. Keating and W.A. Barker, J. Franklin Inst., 274, 253 (1962).
2. M.J. Stephen and G.K. Fraenkel, J. Chem. Phys., 32, 1435 (1960).
3. M.J. Stephen, J. Chem. Phys., 31, 484 (1961).
4. D.D. McCracken, "A Guide to FORTRAN Programming", John Wiley and Sons, Inc., New York (1961).

APPENDIX B

B.1 THE COMPUTER PROGRAM

In the following the program written for evaluating various saturation parameters Ω 's and χ 's in the high temperature case (with linear approximation) and in the infinite temperature case for multilevel-multiresonance systems is presented. It is a FORTRAN program originally written for CDC 3600 Computer and later modified for IBM 7044 Computer. It can analyze several systems in a single run. The dimensional capacity of this program is such that it can analyze systems upto ten levels having maximum of 25 relaxations and 10 pumps. Further, for each system it can analyze a maximum of 5 saturation factors Z_{rs} corresponding to 5 "r,s" pairs of levels. The program consists of the main program "SAT" and three subroutines. The subroutines are subroutine "SELECT", subroutine "ILAIJ" and the subroutine "AIGER". Enough number of comment cards are included in the following listing of the entire program so as to make clear its structure.


```

C(4) MCAL, THE CONTROLLING DATA TO SPECIFY THE NATURE OF THE
C CALCULATIONS TO BE DONE ( IF MCAL=1, ONLY THE INFINITE TEMPERATURE
C CASE CALCULATIONS WILL BE DONE AND IF MCAL=2, BOTH THE INFINITE AND
C FINITE TEMPERATURE CASE CALCULATIONS WILL BE DONE.)
C(5) MPUMP1,MPUMP2, THE TWO LIMITS OF THE TYPE OF THE COMBINATIONS TO BE
C CONSIDERED ( COMBINATIONS CONSIDERED WILL HAVE MINIMUM OF MPUMP1-1
C PUMPS AND MAXIMUM OF MPUMP2-1 PUMPS. ).
C(6) NPARA, THE NUMBER OF THE PARAMETERS OF WHICH THE RELAXATIONS ARE
C LINEAR COMBINATIONS.
C(7) NPAIR, THE NUMBER OF THE 'R,S' PAIRS FOR WHICH CALCULATION OF THE
C SATURATION PARAMETERS KAI'S WILL BE DONE ( IF MCAL=2 ) IN THE
C FINITE TEMPERATURE CASE WITH THE LINEAR APPROXIMATION.
  READ 1,NLEVEL,KRELAX,NPUMP,MCAL,MPUMP1,MPUMP2,NPARA,NPAIR
  FORMAT(8(3X,I3))
  PRINT 1,NLEVEL,KRELAX,NPUMP,MCAL,MPUMP1,MPUMP2,NPARA,NPAIR
  NLESS=NLEVEL-1
  IF(MCAL-1) 6002,6001,6002
C IF MCAL=2, READ ALPHAMERICALLY THE VARIOUS ENERGY GAPS E(I)'S
C WHICH ARE NLEVEL-1 IN NUMBER. THESE ARE USED WHILE GIVING THE
C OUTPUT.
  6002 READ 5,(E(I),I=1,NLESS)
  5   FORMAT(10(1X,A3))
  PRINT 5,(E(I),I=1,NLESS)
C READ ALPHAMERICALLY THE VARIOUS NPARA PARAMETERS L(J)'S WHICH
C CHARACTERIZE THE RELAXATIONS PRESENT IN THE SYSTEM. THESE WILL BE
C USED IN GIVING THE OUTPUT.
  6001 READ 6000,(L(J),J=1,NPARA)
  6000 FORMAT(4(1X,A1))
  PRINT 6000,(L(J),J=1,NPARA)
C READ THE KRELAX RELAXATIONS ( IRF(I)'S ) AND THE COEFFICIENTS
C ( C(I,J)'S ) OF THE VARIOUS L(J) PARAMETERS IN THEM. ( A
C RELAXATION BETWEEN THE 5-TH LEVEL AND THE 7-THLEVEL IS, FOR
C EXAMPLE, READ AS THE FIXED POINT NUMBER '0705'. )
  DO 6 I=1,KRELAX
    READ 7,IRR(I),(C(I,J),J=1,NPARA)

```

```

7  FORMAT(1X,I4,4(3X,F10.6))
6  PRINT 7,IRR(I),(C(I,J),J=1,NPARA)
C  READ THE NPUMP PUMPS ( IPI(I)'S ) ( A PUMP BETWEEN THE 1-ST LEVEL AND
C  THE 4-TH LEVEL IS, FOR EXAMPLE , READ AS THE FIXED POINT NUMBER
C  '0104'. ) READ ALSO THE CHARACTERIZING INDICES ( IPIR(I)'S ) FOR ALL
C  THE PUMPS. IPIR(I)=J IMPLIES THAT THE I-TH PUMP CONNECTS THE SAME
C  PAIR OF LEVELS AS THE J-TH RELAXATION. THIS INFORMATION WILL BE
C  USED TO OUTRIGHTLY REJECT A DISALLOWED COMBINATION HAVING I-TH PUMP
C  AND J-TH RELAXATION WITHOUT TESTING IT BY APPLYING THE RULES OF THE
C  'INSPECTION METHOD'.
C
C  READ 8,(IP(I),IPIR(I),I=1,NPUMP)
8  FORMAT(10(1X,I4,1H(,I2,1H)))
C  PRINT 8,(IP(I),IPIR(I),I=1,NPUMP)
C  IF(MCAL-1) 6006,6007,6006
C  IF MCAL=2, READ THE NPAIR 'R,S' PAIRS OF LEVELS. FOR THE J-TH
C  PAIR 'R' IS READ AS IPAIR(J) AND 'S' IS READ AS JPAIR(J). THESE
C  WILL BE USED IN THE CALCULATION OF KAI'S IN THE HIGH TEMPERATURE
C  CASE WITH LINEAR APPROXIMATION.
C  6006 READ 9,(IPAIR(MPAIR),JPAIR(MPAIR),MPAIR=1,NPAIR)
C  9  FORMAT(10(1X,I2,1H(,I2,1H,))
C  PRINT 9,(IPAIR(MPAIR),JPAIR(MPAIR),MPAIR=1,NPAIR)
C  6007 PRINT 2,NLEVEL
2  FORMAT(//2X48H -* S A T U R A T I O N B E H A V I O U R O F ,I2
/,26H L E V E L S Y S T E M *-)
C  PRINT 81
81  FORMAT(2X76H -----//)
C  NOW READ THE ENERGY LEVEL DIAGRAM.
C  DO 3 I=1,15
C  READ 4
4  FORMAT(80H
/
3  PRINT 4
C  THIS FINISHES THE INPUT.
NMORE=NLEVEL+1
100
101

```

[illegible]

[illegible]

21	GO TO 33		207
	IFF=IEE		208
3006	IF(MRELAX-6) 23,22,23		209
22	NTERM=NTERM+1		210
	LP(NTERM,IAA)=LP(NTERM,IAA)+1		211
	LP(NTERM,IBB)=LP(NTERM,IBB)+1		212
	LP(NTERM,ICC)=LP(NTERM,ICC)+1		213
	LP(NTERM,IDD)=LP(NTERM,IDD)+1		214
	LP(NTERM,IEE)=LP(NTERM,IEE)+1		215
	LP(NTERM,IFF)=LP(NTERM,IFF)+1		216
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)		217
	PRINT 28,NTERM,(L(I),I=1,NPARA)		218
	GO TO 32		219
23	IGG=IFF		220
3007	IF(MRELAX-7) 25,24,25		221
24	NTERM=NTERM+1		222
	LP(NTERM,IAA)=LP(NTERM,IAA)+1		223
	LP(NTERM,IBB)=LP(NTERM,IBB)+1		224
	LP(NTERM,ICC)=LP(NTERM,ICC)+1		225
	LP(NTERM,IDD)=LP(NTERM,IDD)+1		226
	LP(NTERM,IEE)=LP(NTERM,IEE)+1		227
	LP(NTERM,IFF)=LP(NTERM,IFF)+1		228
	LP(NTERM,IGG)=LP(NTERM,IGG)+1		229
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)		230
	PRINT 28,NTERM,(L(I),I=1,NPARA)		231
	GO TO 31		232
25	IHH=IGG		233
3008	IF(MRELAX-8) 27,26,27		234
26	NTERM=NTERM+1		235
	LP(NTERM,IAA)=LP(NTERM,IAA)+1		236
	LP(NTERM,IBB)=LP(NTERM,IBB)+1		237
	LP(NTERM,ICC)=LP(NTERM,ICC)+1		238
	LP(NTERM,IDD)=LP(NTERM,IDD)+1		239
	LP(NTERM,IEE)=LP(NTERM,IEE)+1		240
	LP(NTERM,IFF)=LP(NTERM,IFF)+1		241

242	LP(NTERM,IGG)=LP(NTERM,IGG)+1	242
243	LP(NTERM,IHH)=LP(NTERM,IHH)+1	243
244	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	244
245	PRINT 28,NTERM,(L(I),I=1,NPARA)	245
246	GO TO 30	246
247	III=IHH	247
248	NTERM=NTERM+1	248
249	LP(NTERM,IAA)=LP(NTERM,IAA)+1	249
250	LP(NTERM,IBB)=LP(NTERM,IBB)+1	250
251	LP(NTERM,ICC)=LP(NTERM,ICC)+1	251
252	LP(NTERM,IDD)=LP(NTERM,IDD)+1	252
253	LP(NTERM,IEE)=LP(NTERM,IEE)+1	253
254	LP(NTERM,IFF)=LP(NTERM,IFF)+1	254
255	LP(NTERM,IGG)=LP(NTERM,IGG)+1	255
256	LP(NTERM,IHH)=LP(NTERM,IHH)+1	256
257	LP(NTERM,III)=LP(NTERM,III)+1	257
258	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	258
259	PRINT 28,NTERM,(L(I),I=1,NPARA)	259
260	IF(III-NPARA) 4009,30,4009	260
261	IF(III=III+1	261
262	GO TO 3009	262
263	IF(IHH-NPARA) 4008,31,4008	263
264	IHH=IHH+1	264
265	GO TO 3008	265
266	IF(IGG-NPARA) 4007,32,4007	266
267	IGG=IGG+1	267
268	GO TO 3007	268
269	IF(IFF-NPARA) 4006,33,4006	269
270	IFF=IFF+1	270
271	GO TO 3006	271
272	IF(IEE-NPARA) 4005,34,4005	272
273	IEE=IEE+1	273
274	GO TO 3005	274
275	IF(IDD-NPARA) 4004,35,4004	275
276	IDD=IDD+1	276
27		
3009		
29		
4009		
30		
4008		
31		
4007		
32		
4006		
33		
4005		
34		
4004		

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

C	AND THEN CALL THE SUBROUTINE 'ILAAIJ' WHICH CALCULATES THESE TERM	453
C	COEFFICIENTS.	454
58	DO 4011 I=1,NMORE	455
	DO 4011 J=1,NLEVEL	456
4011	A(I,J)=0.0	457
	CALL ILAAIJ (NLEVEL,NMORE)	458
	CONTINUE	459
C	WE NOW CALL THE SUBROUTINE 'ALGEP' WHICH PERFORMS THE ALGEBRAIC	460
C	CALCULATIONS REQUIRED IN THE EVALUATION OF CONTRIBUTIONS TO THE	461
C	VARIOUS POLYNOMIAL COEFFICIENTS FROM THE ALLOWED COMBINATION.	462
59	CALL ALGEP (NLEVEL,MTERM,NMORE,MCAL,NPAIR,NPARA,MRELAX)	463
C	CALCULATIONS OF THE CONTRIBUTIONS FROM THE ALLOWED COMBINATION TO	464
C	THE APPROPRIATE POLYNOMIAL COEFFICIENTS HAVE BEEN FINISHED.	465
C	NOW GO TO TAKE NEXT SET OF MRELAX RELAXATIONS AND FORM THE NEXT	466
C	COMBINATION.	467
60	GO TO (69,68,67,66,65,64,63,62,61),MRELAX	468
61	IF(JI-NK9) 71,62,71	469
71	JI=JI+1	470
	GO TO 1009	471
62	IF(JH-NK8) 72,63,72	472
72	JH=JH+1	473
	GO TO 1008	474
63	IF(JG-NK7) 73,64,73	475
73	JG=JG+1	476
	GO TO 1007	477
64	IF(JF-NK6) 74,65,74	478
74	JF=JF+1	479
	GO TO 1006	480
65	IF(JE-NK5) 75,66,75	481
75	JE=JE+1	482
	GO TO 1005	483
66	IF(JD-NK4) 76,67,76	484
76	JD=JD+1	485
	GO TO 1004	486
67	IF(JC-NK3) 77,68,77	487

[illegible]

```

C HAD MRELAX BEEN EQUAL TO ZERO WE WOULD HAVE GONE DIRECTLY TO
C STATEMENT NUMBER 219 TO TAKE THE NEXT SET OF MPUMP PUMPS. IN SUCH A
C CASE THERE IS NO OUTPUT TO BE GIVEN EXCEPT THE SET OF MPUMP
C PJMPS WHICH CONSTITUTE ANALLOWED COMBINATION. THIS HAS ALREADY BEEN
C PRINTED.
C PRINT THE NUMBER OF ALLOWED AND DISALLOWED COMBINATIONS.
85 PRINT 97,NGOOD,NBAD
   NGOOD=0
   NBAD=0
   PRINT 98
   PRINT 115
115 FORMAT(21H NUMERATOR FOR OMEGA=//)
C IN THIS DO LOOP (DO 116) WE PRINT NONZERO BETA'S.
   DO 116 NTERM=1,MTERM
   BETA(NTERM)=(BETA(NTERM))*((6.0)**(MRELAX-LP(NTERM,2)-LP(NTERM,3)))
   /)
   IF(BETA(NTERM)) 5008,116,5008
5008 PRINT 101,NTERM,BETA(NTERM)
116 CONTINUE
C IF MCAL=1, NO MORE OUTPUT REMAINS TO BE GIVEN AND THEREFORE GO TO
C TAKE NEXT SET OF MPUMP PUMPS. HOWEVER, IF MCAL=2, GO BELOW TO GIVE
C THE OUTPUT FOR THE HIGH TEMPERATURE CASE AS WELL.
   GO TO (219,117),MCAL
117 PRINT 103
   PRINT 115
   PRINT 104,(E(I),I=1,NLESS)
   PRINT 4015
C IN THIS DO LOOP (DO 118) WE PRINT NONZER XD'S.
   DO 118 NTERM=1,MTERM
   J=1
5009 IF(XD(NTERM,J)) 5012,5010,5012
5010 IF(J-NLEVEL) 5011,118,118
5011 J=J+1
   GO TO 5009
5012 PRINT 106,NTERM,(XD(NTERM,J),J=1,NLEVEL)

```

[illegible]

[illegible]

```

1  $IBFTC SUB1  NODECK
2  SUBROUTINE SELECT (NLEVEL,NLESS,LOOP)
3  C
4  C THE SUBROUTINE 'SELECT'
5  C THIS SUBROUTINE HAS BEEN WRITTEN FOLLOWING THE RULES OF THE METHOD
6  C OF INSPECTION FOR TESTING WETHER A PARTICULAR COMBINATION IS
7  C ALLOWED OR NOT. WE COME HERE FROM THE MAIN PROGRAM WITH THE VALUE
8  C LOOP=0 AND IF WE FIND HERE THAT THE COMBINATION DOES NOT FULFILL
9  C THE RULES OF THE INSPECTION METHOD THAT IS IT IS NOT ALLOWED WE SET
10 C LOOP=1 AND RETURN TO THE MAIN PROGRAM. IF ON THE OTHER HAND THE
11 C COMBINATION IS FOUND TO BE ALLOWED WE RETURN TO THE MAIN PROGRAM
12 C WITHOUT ALTERING THE VALUE OF 'LOOP'.
13 C MOST OF THE INFORMATION TO THIS SUBROUTINE COMES FROM THE COMMON
14 C STORAGE AREA.
15 C HERE THE RELAXATIONS AND/OR PUMPS PRESENT IN THE COMBINATION ARE
16 C ALL SPLIT INTO TWO NUMBERS ( ISUB(I)'S AND JSUB(I)'S ) WHICH
17 C DETERMINE THE TWO LEVELS WHICH IT COUPLES. ACTUALLY THESE NUMBERS
18 C ARE UTILIZED HERE TO FIND OUT WETHER THE COMBINATION IS ALLOWED OR
19 C NOT. ISUB(I)'S AND JSUB(I)'S ARE ALSO USED FOR FINDING OUT THE TERM
20 C COEFFICIENTS A(I,J)'S FOR THE COMBINATION AND HENCE THESE ARE
21 C STORED HERE IN A COMMON STORAGE AREA FOR USING IN THE SUBROUTINE
22 C 'ILAAIJ'.
23 C
24 C DIMENSION LP(220,4),B(25,4),BETA(220),XD(220,10),XNR(220,10,5),A(1
25 C /1,10),ISUB(9),JSUB(9),IQ(9),IQR(9),IPAIR(5),JPAIR(5)
26 C DIMENSION IB(9),KTWO(9)
27 C COMMON LP,B,BETA,XD,XNR,A,ISUB,JSUB,IQ,IQR,IPAIR,JPAIR
28 C DO 7 L=1,NLESS
29 C MM=100
30 C IF(IQ(L)-100-MM) 5,4,4
31 C MM=MM+100
32 C GO TO 3
33 C ISUB(L)=MM/100
34 C JSUB(L)=IQ(L)-MM
35 C 7 CONTINUE
36 C I=1
37 C 10 DO 11 J=1,NLESS
38 C 11 IB(J)=1

```

IB(I)=0	35
KM=1	36
NK2=1	37
KTWO(KM)=ISUB(I)	38
12 K2=KTWO(KM)	39
93 II=1	40
99 IF(IB(II)) 13,92,13	41
92 II=II+1	42
IF(II-NLEVEL) 99,21,21	43
13 IF(ISUB(II)-K2) 15,14,15	44
14 K2=JSUB(II)	45
GO TO 17	46
15 IF(JSUB(II)-K2) 18,16,18	47
16 K2=ISUB(II)	48
17 IB(II)=0	49
KM=KM+1	50
NK2=NK2+1	51
KTWO(KM)=K2	52
GO TO 93	53
18 II=II+1	54
IF(II-NLEVEL) 99,21,21	55
19 IF(KM-1) 20,28,20	56
20 KM=KM-1	57
NK2=NK2-1	58
30 TO 12	59
21 IF(NK2-3) 19,22,23	60
22 IF(KTWO(NK2)-JSUB(I)) 19,29,19	61
23 IF(KTWO(NK2)-JSUB(I)) 24,29,24	62
24 NN=1	63
25 IF(KTWO(NK2)-KTWO(NN)) 26,29,26	64
26 NN=NN+1	65
IF((NK2-NN)-3) 19,25,25	66
28 I=I+1	67
IF(I-NLEVEL) 10,30,30	68
29 LOOP=1	69
30 RETURN	70
	71

[illegible]

[illegible]

[illegible]

(B28)

[illegible]

(B28)

```

1  $IBFTC SUB3      NODECK
2  SUBROUTINE ALGEBR (NLEVEL,MTERM,NMORE,MCAL,NPAIR,NPARA,MRELAX)
3  C THE SUBROUTINE 'ALGEBR'
4  C THIS SUBROUTINE IS CALLED FOR EVERY ALLOWED COMBINATION FOR WHICH
5  C IT CALCULATES THE CONTRIBUTIONS TO DESIRED POLYNOMIALS ( BETA'S ,IF
6  C MCAL=1 OR BETA'S ,XD'S AND XNR'S ,IF MCAL=2 ).
7  C IT OBTAINS MOST OF THE INFORMATION FROM THE COMMON STORAGE AREA.
8  C ACTUALLY HERE WE MULTIPLY THE RELAXATIONS PRESENT IN THE ALLOWED
9  C COMBINATION. THIS MULTIPLICATION WILL BE SIMPLE IN THE INFINITE
10 C TEMPERATURE CASE CALCULATIONS BECAUSE THE POLYNOMIALS WILL THEN
11 C CONTAIN NUMERICAL COEFFICIENTS ONLY. HOWEVER, IN CASE MCAL=2, THE
12 C HIGH TEMPERATURE CASE CALCULATIONS ARE ALSO TO BE DONE AND IN THIS
13 C CASE THE POLYNOMIALS CONTAIN AS THE COEFFICIENTS THE LINEAR
14 C COMBINATIONS OF THE VARIOUS ENERGY GAPS E(J)'S.
15 C DIMENSION LP(220,4),B(25,4),BETA(220),XD(220,10),XNR(220,10,5),A(1
16 C /1,10),ISUB(9),JSUB(9),IQ(9),IQR(9),IPAIR(5),JPAIR(5)
17 C DIMENSION ALPHA(220),LLP(4)
18 C COMMON LP,B,BETA,XD,XNR,A,ISUB,JSUB,IQ,IQR,IPAIR,JPAIR
19 C IN THIS DO LOOP (DO 2000) WE SET ALL ALPHA'S CORRESPONDING TO THIS
20 C COMBINATION EQUAL TO ZERO.
21 C DO 2000 NTERM=1,MTERM
22 C 2000 ALPHA(NTERM)=0.0
23 C IN THIS DO LOOP (DO 2001) WE INITIALISE ALL LLP'S TO ZERO. FOR A
24 C PARTICULAR PSEUDO TERM OF THE PRODUCT, LLP(I) WILL GIVE THE POWER
25 C OF THE 'RELAXATION COEFFICIENT L(I)'.
26 C DO 2001 I=1,NPARA
27 C 2001 LLP(I)=0
28 C UTILIZING THE VALUES OF IQR(I)'S FROM THE COMMON STORAGE AREA WE
29 C NOW SET IN IA,IB,IC,ID,.....ETC. THE INDICES 'I' 'S OF THE MRELAX
30 C RELAXATIONS ( IR(I)'S ) PRESENT IN THE ALLOWED COMBINATION.
31 C GO TO (1,2,3,4,5,6,7,8,9),MRELAX
32 C 9 II=IQR(9)
33 C 8 IH=IQR(8)
34 C 7 IG=IQR(7)
35 C 6 IF=IQR(6)

```

[illegible]

86	IF(B(ID,JD)) 17,66,17	69
17	CONS4=CONS3*B(ID,JD)	70
	IF(MRELAX-4) 18,54,18	71
54	CONS=CONS4	72
	LLP(JA)=LLP(JA)+1	73
	LLP(JB)=LLP(JB)+1	74
	LLP(JC)=LLP(JC)+1	75
	LLP(JD)=LLP(JD)+1	76
	GO TO 28	77
18	JE=1	78
85	IF(B(IE,JE)) 19,65,19	79
19	CONS5=CONS4*B(IE,JE)	80
	IF(MRELAX-5) 20,55,20	81
55	CONS=CONS5	82
	LLP(JA)=LLP(JA)+1	83
	LLP(JB)=LLP(JB)+1	84
	LLP(JC)=LLP(JC)+1	85
	LLP(JD)=LLP(JD)+1	86
	LLP(JE)=LLP(JE)+1	87
	GO TO 28	88
20	JF=1	89
84	IF(B(IF,JF)) 21,64,21	90
21	CONS6=CONS5*B(IF,JF)	91
	IF(MRELAX-6) 22,56,22	92
56	CONS=CONS6	93
	LLP(JA)=LLP(JA)+1	94
	LLP(JB)=LLP(JB)+1	95
	LLP(JC)=LLP(JC)+1	96
	LLP(JD)=LLP(JD)+1	97
	LLP(JE)=LLP(JE)+1	98
	LLP(JF)=LLP(JF)+1	99
	GO TO 28	100
22	JG=1	101
83	IF(B(IG,JG)) 23,63,23	102
23	CONS7=CONS6*B(IG,JG)	103

57	IF(MRELAX-7) 24,57,24	104
	CONS=CONS7	105
	LLP(JA)=LLP(JA)+1	106
	LLP(JB)=LLP(JB)+1	107
	LLP(JC)=LLP(JC)+1	108
	LLP(JD)=LLP(JD)+1	109
	LLP(JE)=LLP(JE)+1	110
	LLP(JF)=LLP(JF)+1	111
	LLP(JG)=LLP(JG)+1	112
	GO TO 28	113
24	JH=1	114
82	IF(B(IH,JH)) 25,62,25	115
25	CONS8=CONS7*B(IH,JH)	116
	IF(MRELAX-8) 26,58,26	117
58	CONS=CONS8	118
	LLP(JA)=LLP(JA)+1	119
	LLP(JB)=LLP(JB)+1	120
	LLP(JC)=LLP(JC)+1	121
	LLP(JD)=LLP(JD)+1	122
	LLP(JE)=LLP(JE)+1	123
	LLP(JF)=LLP(JF)+1	124
	LLP(JG)=LLP(JG)+1	125
	LLP(JH)=LLP(JH)+1	126
	GO TO 28	127
26	JI=1	128
81	IF(B(II,JI)) 27,61,27	129
27	CONS=CONS8*B(II,JI)	130
	LLP(JA)=LLP(JA)+1	131
	LLP(JB)=LLP(JB)+1	132
	LLP(JC)=LLP(JC)+1	133
	LLP(JD)=LLP(JD)+1	134
	LLP(JE)=LLP(JE)+1	135
	LLP(JF)=LLP(JF)+1	136
	LLP(JG)=LLP(JG)+1	137
	LLP(JH)=LLP(JH)+1	138

[illegible]

```

175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209

78 JC=JC+1
79 GO TO 87
68 IF(JB-NPARA) 79,69,79
79 JB=JB+1
GO TO 88
69 IF(JA-NPARA) 80,70,80
80 JA=JA+1
GO TO 89
C WE ARE HERE ( STATEMENT NUMBER 70 ) SINCE ALL PSEUDO TERMS HAVE
C BEEN CONSIDERED AND ALL ALPHA'S HAVE BEEN DETERMINED. WE NOW 'ADD-
C STORE'. THESE ALPHA'S IN BETA'S WHICH WILL GIVE THE FINAL POLYNOMIAL
C COEFFICIENTS IN THE INFINITE TEMPERATURE CASE, OF COURSE ONLY AFTER
C ALL THE ALLOWED COMBINATIONS HAVE BEEN CONSIDERED AND THEIR
C CONTRIBUTIONS ( ALPHA'S ) HAVE BEEN ADDED TO BETA'S.
70 DO 90 NTERM=1,MTERM
90 BETA(NTERM)=BETA(NTERM)+ALPHA(NTERM)
C NOW IF MCAL=1, NO MORE CALCULATION REMAINS TO BE DONE IN THIS
C SUBROUTINE AND HENCE WE RETURN TO THE MAIN PROGRAM. HOWEVER, IF
C MCAL=2, WE HAVE TO PERFORM THE HIGH TEMPERATURE CASE CALCULATIONS
C ALSO. HENCE IN THIS CASE WE GO TO STATEMENT NUMBER 91 WHERE IN THE
C DO LOOPS (DO 92) WE EVALUATE AND 'ADD-STORE' THE CONTRIBUTIONS TO
C ALL THE REQUIRED COEFFICIENTS ( XD'S AND XNR'S ) OF THE POLYNOMIALS
C IN THE HIGH TEMPERATURE CASE. HERE WE MAKE USE OF THE TERM
C COEFFICIENTS A(I,J)'S EVALUATED IN THE SUBROUTINE 'ILAAIJ'.
GO TO (94,91),MCAL
91 DO 92 NTERM=1,MTERM
DO 92 J=1,NLEVEL
XD(NTERM,J)=XD(NTERM,J)+ALPHA(NTERM)*A(NMORE,J)
DO 92 MPAIR=1,NPAIR
NR=IPAIR(MPAIR)
NS=JPAIR(MPAIR)
92 XNR(NTERM,J,MPAIR)=XNR(NTERM,J,MPAIR)+(ALPHA(NTERM))*(A(NS,J)-A(NR
/,J))
94 RETURN
END
$ENTRY

```

B.3 THE CORRESPONDING OUTPUT

As specified by the data, the program calculates the saturation parameters $\Omega_1, \Omega_2, \Omega_1^\infty, \Omega_2^\infty, \chi_1^{04-03}, \chi_2^{04-03}, \Omega_{1,2}^\infty, \Omega_{1,2}^{04-03}$ and $\chi_{1,2}^{04-03}$. It may be noted here that since the first pump corresponds to the pair "r,s" (04-03) we have χ_1^{04-03} and $\chi_{1,2}^{04-03}$ both equal to zero. This can be seen in the output where no term exists in the corresponding numerator of these saturation parameters.

---* S A T U R A T I O N B E H A V I O U R O F 4 L E V E L S Y S T E M *---

ONE NUCLEUS(I=1/2)
AND ONE ELECTRON

MI=-1/2	-----4	MS=+1/2
MI=+1/2	-----3	

MI=-1/2	-----2	MS=-1/2
MI=+1/2	-----1	

SUMS OVER TERMS CONTAINING 0 PUMP/PUMPS

VARIOUS TERMS IN
THE POLYNOMIALS
ARE OF THE
FOLLOWING TYPE

3 0 0
 1-K L M
 2 1 0
 2-K L M
 2 0 1
 3-K L M
 1 2 0
 4-K L M
 1 1 1
 5-K L M
 1 0 2
 6-K L M
 0 3 0
 7-K L M
 0 2 1
 8-K L M
 0 1 2
 9-K L M
 0 0 3
 10-K L M

16
4

. ALLOWED COMBINATIONS=
 DISALLOWED COMBINATIONS=

INFINITE TEMPERATURE CASE

COMMON DENOMINATOR FOR ALL OMEGA S=

1	0.37499878E 02
2	0.25145710E-07
3	0.27499935E 02
4	-0.12499980E 01
6	0.49999920E 01

FINIIF TEMPERATURE CASE WITH LINEAR APPROXIMATION

COMMON DENOMINATOR FOR ALL OMEGA S=

	E12	E23	E34
1-	0.69444E 00-0.52083E 00-0.65972E 00-0.52083E 00		
2-	0.27940E-08-0.93132E-09-0.46566E-09 0.34722E 00		
3-	0.30555E 01-0.22917E 01-0.32500E 01-0.22917E 01		
4-	-0.83333E 00 0.62500E 00 0.10000E 01 0.62500E 00		
6-	0.33333E 01-0.25000E 01-0.40000E 01-0.25000E 01		

COMMON DENOMINATOR FOR ALL (KAI) S=

	E12	E23	E34
1-	0.	-0.	0.17361E 00

01	004	006	002	002	001	003	003	001
E12 E23 E34								
K L M								
0403		+00.250000		+00.000000		+00.000000		+00.000000
0402		+00.250000		-00.500000		+01.000000		+01.000000
0401		+00.166666		+00.000000		+00.000000		+00.000000
0302		+00.166666		+00.000000		+00.000000		+01.000000
0301		+00.250000		+00.500000		+00.500000		+00.000000
0201		+00.250000		+00.000000		+00.000000		+00.000000
0304(01) 0102(06)								
04-03,								

ONE NUCLEUS(I=1/2)
AND ONE ELECTRON

MI=-1/2	-----4	MS=+1/2
MI=+1/2	-----3	

MI=-1/2	-----2	MS=-1/2
MI=+1/2	-----1	

8
2

ALLOWED COMBINATIONS=
DISALLOWED COMBINATIONS=

INFINITE TEMPERATURE CASE

NUMERATOR FOR OMEGA=

1	0.13749968E 02
2	0.55879354E-08
3	0.79999919E 01
4	-0.25000000E 00
6	0.10000000E 01

FINITE TEMPERATURE CASE WITH LINEAR APPROXIMATION

NUMERATOR FOR OMEGA=

	E12	E23	E34
1-	0.15278E 01-0.11458E 01-0.14583E 01-0.72916E 00		
2-	0.37253E-08-0.37253E-08-0.	0.75000E 00	
3-	0.53333E 01-0.40000E 01-0.60000E 01-0.30000E 01		

4- -0.10000E 01 0.75000E 00 0.15000E 01 0.75000E 00
 6- 0.40000E 01-0.30000E 01-0.60000E 01-0.30000E 01

NUMERATOR FOR (KAI) $\frac{4-3}{=}$

E12 E23 E34

WHEN PUMP/PUMPS PRESENT IS/ARE 102,

ALLOWED COMBINATIONS= 8
 DISALLOWED COMBINATIONS= 2

INFINITE TEMPERATURE CASE

NUMERATOR FOR OMEGA=

1 0.13749968E 02
 3 0.79999918E 01
 4 -0.25000000E 00
 6 0.10000000E 01

FINITE TEMPERATURE CASE WITH LINEAR APPROXIMATION

NUMERATOR FOR OMEGA=

	E12	E23	E34
1- 0.15278E	01-0.38194E	00-0.76389E	00-0.79861E 00
2- 0.	-0.41667E	00-0.	0.50000E 00
3- 0.53333E	01-0.13333E	01-0.26667E	01-0.23333E 01
4- -0.10000E	01 0.25000E	00 0.50000E	00 0.25000E 00
6- 0.40000E	01-0.10000E	01-0.20000E	01-0.10000E 01

NUMERATOR FOR (KAI) $\frac{4}{3} =$

	E12	E23	E34
1- 0.	-0.34722E-01-0.		0.38194E 00
3- 0.	-0.50000E 00-0.		0.13333E 01
4- 0.	0.25000E 00-0.		-0.25000E 00
6- 0.	-0.10000E 01-0.		0.10000E 01

SUMS OVER TERMS CONTAINING 2 PUMP/PUMPS

SUMMARY

SUMMARY

A theoretical analysis of the saturation phenomena in multilevel multiresonance Zeeman systems employing the rate-equation approach has been given here. While a quantum-mechanical description of such systems utilizes the density matrix formalism, the conventional rate-equation approach assumes that the off-diagonal elements of the density matrix are zero and thus considers the rate of change ^{of} the diagonal elements only. This assumption, that is, the use of the rate-equations, is valid in many cases and leads to a simpler description. Most of the work reported here was completed before the publication of the recent work of Freed on saturation in electron spin resonance based on density matrix formalism.

It has been shown that the rate-equation approaches of Stephen and Fraenkel (the Diagram Method) and Keating and Barker (the Inspection Method) are actually equivalent. The "diagram method" was originally developed for the study of saturation in multilevel-multiresonance Zeeman systems mainly in the 'infinite temperature approximation', while the "inspection method" was formulated for obtaining normalised steady state finite temperature population distribution in such systems. It has been found that the application of the diagram method for the study of saturation in multilevel-multiresonance systems is complicated both at finite temperature and high temperature. In order to develop a simpler procedure for the study of saturation in such systems at "finite temperatures" and at "high temperatures", the inspection method has been employed here. A finite temperature expression for the saturation factor Z_{rs} in terms of t solutions thus obtained by the inspection method yields on analysis, general finite temperature expressions for the saturation parameters Ω 's and χ .

These are found to be functions of (1) the various relaxations present in the system, (2) the energy-gaps between the adjacent energy levels of the system and (3) temperature T of the system. The infinite temperature and high temperature expressions for the saturation parameters obtained by Stephen and Fraenkel have been rederived by taking proper limits (for $T \rightarrow 0$ or T high) in the various terms of the finite temperature expressions obtained in the present work. These rederived expressions, in general, agree with those of Stephen and Fraenkel but there are certain discrepancies which have been pointed out. Use of the finite temperature expressions for the saturation parameters obtained here have also been demonstrated by presenting a sample calculation in a four-level odd electron ($s=\frac{1}{2}$) — spin-half nucleus ($I=\frac{1}{2}$) coupled system. An expression for the m_I dependence of the saturation parameter Ω_{pq}^{∞} on the magnetic quantum number m_I has been obtained for the e.s.r. lines of free radicals in solution and found to agree with experimental data. It has also been shown that the expression obtained by Stephen and Fraenkel for the m_I dependence of Ω_{pq}^{∞} is a particular form of the expression obtained here.

Assuming that the various relaxations present in the system are available as linear combinations of certain parameters characterizing the relaxation mechanisms present in it, the expressions for the saturation parameters have been modified in the infinite temperature and high temperature case. The final form of the expressions thus obtained have been adopted for machine computations of the saturation parameters. Examples of machine computation of the various saturation parameters in a six-level and a ten-level system have been presented. The infinite

temperature results are compared with the results of similar calculations done by Stephen and Fraenkel. The FORTRAN program written for this purpose has also been presented in an Appendix.

It is hoped that the present formalism for the saturation studies in multilevel-multiresonance systems and the associated computer program developed here will help considerably in the calculations for many-level systems which are otherwise formidable. In turn, the results of such calculations can be used in the investigation of relaxation processes present in a system.

VITAE

K.M.S. Saxena was born on June 26, 1939 in Lucknow, Uttar Pradesh. After receiving his early education from Hobart Triloknath Intermediate College, Tanda, Faizabad, Uttar Pradesh, he joined the University of Lucknow in July 1955. He received his B.Sc., B.Sc. (Honours) and M.Sc. (Physics) degrees from this University in the years 1958, 1959 and 1960. He was later a Lecturer in Physics at the Shia College, Lucknow University, Lucknow and Meerut College, Agra University, Agra. He subsequently joined the Ph.D. program in the Physics Department at Indian Institute of Technology, Kanpur, where he has been a Research Assistant since November 1961 sharing teaching responsibilities.

FINITE TEMPERATURE CASE WITH LINEAR APPROXIMATION

NUMERATOR FOR OMEGA=

	E12	E23	E34
1- 0.3333E 01-0.83333E 00-0.16667E 01-0.83333E 00			
2- 0. -0.10000E 01-0. 0.10000E 01			
3- 0.80000E 01-0.20000E 01-0.40000E 01-0.20000E 01			

NUMERATOR FOR (KAI) ^{4- 3} =

E12	E23	E34
-----	-----	-----

(B46)

14	NTERM=NTERM+1	172
	LP(NTERM,IAA)=LP(NTERM,IAA)+1	173
	LP(NTERM,IBB)=LP(NTERM,IBB)+1	174
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	175
	PRINT 28,NTERM,(L(I),I=1,NPARA)	176
	GO TO 36	177
15	ICC=IBB	178
3003	IF(MRELAX-3) 17,16,17	179
16	NTERM=NTERM+1	180
	LP(NTERM,IAA)=LP(NTERM,IAA)+1	181
	LP(NTERM,IBB)=LP(NTERM,IBB)+1	182
	LP(NTERM,ICC)=LP(NTERM,ICC)+1	183
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	184
	PRINT 28,NTERM,(L(I),I=1,NPARA)	185
	GO TO 35	186
17	IDD=ICC	187
3004	IF(MRELAX-4) 19,18,19	188
18	NTERM=NTERM+1	189
	LP(NTERM,IAA)=LP(NTERM,IAA)+1	190
	LP(NTERM,IBB)=LP(NTERM,IBB)+1	191
	LP(NTERM,ICC)=LP(NTERM,ICC)+1	192
	LP(NTERM,IDD)=LP(NTERM,IDD)+1	193
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	194
	PRINT 28,NTERM,(L(I),I=1,NPARA)	195
	GO TO 34	196
19	IEE=IDD	197
3005	IF(MRELAX-5) 21,20,21	198
20	NTERM=NTERM+1	199
	LP(NTERM,IAA)=LP(NTERM,IAA)+1	200
	LP(NTERM,IBB)=LP(NTERM,IBB)+1	201
	LP(NTERM,ICC)=LP(NTERM,ICC)+1	202
	LP(NTERM,IDD)=LP(NTERM,IDD)+1	203
	LP(NTERM,IEE)=LP(NTERM,IEE)+1	204
	PRINT 4000,(LP(NTERM,I),I=1,NPARA)	205
	PRINT 28,NTERM,(L(I),I=1,NPARA)	206

```

523 103 FORMAT(///50H FINITE TEMPERATURE CASE WITH LINEAR APPROXIMATION///
524 //)
525 PRINT 99
526 PRINT 104,(E(I),I=1,NLESS)
527 FORMAT(/18X,9(4X,A3,5X),/)
528 104 PRINT 4015
529 4015 FORMAT(//)
530 IN THIS DO LOOP (DO 105) PRINTS NONZERO XD'S.
531 DO 105 NTERM=1,MTERM
532 J=1
533 5017 IF(XD(NTERM,J)) 5020,5018,5020
534 5018 IF(J-NLEVEL) 5019,105,105
535 5019 J=J+1
536 GO TO 5017
537 5020 PRINT 106,NTERM,(XD(NTERM,J),J=1,NLEVEL)
538 106 FORMAT(1X,13,2H- ,10E12.5)
539 105 CONTINUE
540 IN THIS DO LOOP (DO 109) WE TAKE ONE BY ONE ALL THE 'NPAIR' PAIRS
541 OF LEVELS 'R,S' FOR PRINTING THE CORRESPONDING XNR'S.
542 DO 109 MPAIR=1,NPAIR
543 PRINT 107,IPAIR(MPAIR),JPAIR(MPAIR)
544 107 FORMAT(//32X,I2,1H-,I2)
545 PRINT 108
546 108 FORMAT(41H COMMON DENOMINATOR FOR ALL (KAI) S=//)
547 PRINT 104,(E(I),I=1,NLESS)
548 PRINT 4015
549 FOR MPAIR-TH PAIR THIS DO LOOP (DO 109) PRINTS NONZERO XNR'S.
550 DO 109 NTERM=1,MTERM
551 J=1
552 5004 IF(XNR(NTERM,J,MPAIR)) 5007,5005,5007
553 5005 IF(J-NLEVEL) 5006,109,109
554 5006 J=J+1
555 GO TO 5004
556 5007 PRINT 106,NTERM,(XNR(NTERM,J,MPAIR),J=1,NLEVEL)
557 109 CONTINUE

```

39	IF(JJ(I)-0) 40,41,40	104
40	I=I+1	105
	IF(I-NLEVEL) 39,67,67	106
41	L=2	107
42	IF(IB(L)-0) 63,43,63	108
43	IF(ISUB(I)-L) 53,44,53	109
44	K2=JSUB(I)	110
	IF(K2-L) 47,45,45	111
45	DO 46 J=1,NLEVEL	112
46	A(K2,J)=A(L,J)	113
	IB(K2)=0	114
	K=K-1	115
	GO TO 64	116
47	DO 48 J=1,K2	117
48	A(K2,J)=A(L,J)	118
	J1=K2+1	119
	DO 49 J=J1,L	120
49	A(K2,J)=A(L,J)+1.0	121
	IF(L-NLEVEL) 50,52,52	122
50	J1=L+1	123
	DO 51 J=J1,NLEVEL	124
51	A(K2,J)=A(L,J)	125
52	IB(K2)=0	126
	K=K-1	127
	GO TO 64	128
53	IF(JSUB(I)-L) 63,54,63	129
54	K2=ISUB(I)	130
	IF(K2-L) 61,55,55	131
55	DO 56 J=1,L	132
56	A(K2,J)=A(L,J)	133
	J1=L+1	134
	DO 57 J=J1,K2	135
57	A(K2,J)=A(L,J)-1.0	136
	IF(K2-NLEVEL) 58,60,60	137
58	J1=K2+1	138